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QUANTUM MECHANICS AND RADIOACTIVE DISINTEGRATION[1]

By R. W. Gurney and E. U. Condon

Abstract

Application of quantum mechanics to a simple model of the nucleus gives the phenomenon of radioactive disintegration. The statistical nature of the quantum mechanics gives directly disintegration as a chance phenomenon without any special hypothesis. §1 contains a presentation of those features of quantum mechanics which are here used and gives a simple calculation of the disintegration constant. §2 discusses the qualitative application of the model to the nucleus. §3 presents quantitative calculations amounting to a theoretical interpretation of the Geiger-Nuttall relation between the rate of disintegration and the energy of the emitted α-particle. In getting this relation one arrives at the rather remarkable conclusion that the law of force between emitted α-particle and the rest of the nucleus is substantially the same in all the atoms even where the decay rates stand in the ratio 10^{22}. §4 calls attention to the natural way in which the paradoxical results of Rutherford and Chadwick on the scattering of fast α-particles by uranium receive explanation with the model here used. §5 discusses certain limitations inherent in the methods employed.

THE study of radioacitivity itself together with the application of it as a working source of high speed helium nuclei and electrons has played a fundamental role in the development of quantum physics. The scattering experiments of Rutherford and his associates gave the picture of the nuclear atom on which all of the success of modern atomic theory depends. Bohr's formulation of quantum postulates to be applied to such a model was a great step in the extension of knowledge of atomic structure and finally culminated in 1925 in the discovery by Heisenberg and by Schrödinger of a reformulation of mechanical laws which has subsequently proved extremely powerful in handling atomic structure problems. In this development of the last fifteen years little advance has been made on the problem of the structure of the nucleus.

It seems, however, that the new quantum mechanics has had sufficient success to justify the hope that it is competent to carry out an effective attack on the problem. The quantum mechanics has in it just those statistical elements which would seem appropriate to an explanation of the phenomenon

[1] An account of this work was first published in Nature for September 22, 1928. In a number of the Zeitschrift für Physik (**51**, 204, 1928) received here two weeks ago there appears a paper by Gamow who has arrived quite independently at the same basic idea as was presented in our letter and which is here treated in detail. Reports of this paper were also given at the Schenectady meeting of the National Academy of Sciences on November 20, 1928 and at the Minneapolis meeting of the American Physical Society on December 1, 1928.

of radioactive decay. This is the feature of the general problem with which we are concerned in this paper. We believe that the results provide at last an interpretation of nuclear disintegration which in its fundamental points is very close to the truth although it is necessarily quite incomplete.

The outstanding difficulties in the way of a good theoretical treatment of nuclear structure at present are mainly bound up with our lack of understanding of the quantum mechanics of the magnetism of the fundamental particles. This question has been much advanced this year by Dirac's extension of Pauli's theory of the spinning electron[2] but this remains essentially a theory of the behavior of one electron in an electromagnetic field. Not only is it apparently still unsatisfactory as such but this limitation must necessarily be disposed of in principle before the many body nuclear problem can be approached. And with that done there will remain the inevitable analytical difficulties.

Enough is known, however, to teach us that probably the magnetic interaction is not to be handled simply by an alteration of a potential energy function depending solely on the coordinates of the several interacting particles. This tends to detract from the value of arguments based simply on the use of quantum mechanics with the positional coordinates of the nuclear constituents. Nevertheless we shall restrict ourselves to the use of such methods in the discussion of the instability or capacity for spontaneous disintegration of a very much simplified nuclear model. The simplification to be made will consist in supposing that we can discuss the behavior of any one constituent by applying the quantum mechanics to it as a single body moving in a force field due to the rest of the nucleus.

The difference between quantum mechanics and classical mechanics which is here made responsible for the disintegration process is easily stated. In classical mechanics the orbit of a particle is entirely confined to those points in space at which its potential energy is less than its total energy. This is not true in quantum mechanics. Classically if a particle be moving in a basin of low potential energy and have not as much total energy as the maximum of potential energy surrounding the basin, it must *certainly* remain there for all time, unless it acquires the deficiency in energy somehow. But in quantum mechanics most statements of certainty are replaced by statements of probability. And the above statement must now be altered to read " · · · it may remain there for a long time but as time goes on the probability that it has escaped, even without change in its total energy, increases toward unity."

In §1 of this paper the detailed development of the argument leading to the conclusion of the preceding paragraph is given. In §2 we discuss its qualitative application to the nuclear disintegration problem. §3 is devoted to semi-quantitative estimates of the rates of decay.

1. Coupling of Motions of Equal Energy

Consider a particle of mass μ. It is sufficient to consider one degree of freedom; let the coordinate of the particle be x and let the forces be measured by the potential energy function $V(x)$.

[2] Dirac, Proc. Roy. Soc. **A117**, 610; **A118**, 351 (1928).

In classical mechanics the equations of motion possess the energy integral

$$p^2/2\mu+V(x)=W \tag{1}$$

(p = momentum) which, for values of x such that $W-V(x)<0$, can only be satisfied by p pure imaginary. Therefore, classically, one had the result that a particle could only be where $W-V(x)\geqq 0$. An important consequence of this was that if there were several ranges of x for which $W-V(x)\geqq 0$ separated by ranges where $W-V(x)<0$, then there were several different motions possible with the energy level W, each of which was wholly confined to one of these separate ranges. Thus in Fig. 1 for the energy level indicated there would be two distinct types of motion of the same energy W; one is a libration in the range I, and the other a libration in the range II.

These results are modified considerably by the new quantum mechanics. In the first place, Eq. (1) loses its validity and is replaced by an integral theorem, as Born[3] has shown, in which there is no longer a definite correlation between simultaneous value of position and momentum as (1) implies. The quantum mechanical form of (1) is, if $\psi(x)$ is Schroedinger's wave function

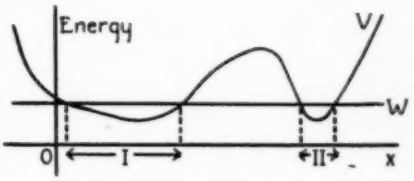

Fig. 1.

$$W=\int_{-\infty}^{+\infty}\left(\frac{h^2}{8\pi^2\mu}\frac{d\psi}{dx}\frac{d\bar{\psi}}{dx}+V(x)\psi\bar{\psi}\right)dx \tag{1a}$$

The lack of a precise correlation has been much emphasized by Heisenberg and by Bohr,[4] and is a general characteristic of quantum mechanics. From the new standpoint, one has to consider the behavior of Schrödinger's equation for the problem

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2\mu}{h^2}(W-V(x))\psi=0. \tag{2}$$

As is well known, in some problems there are solutions $\psi(W, x)$ for certain values of W which are finite and continuous everywhere. These are the "allowed" values of quantum theory. For the $\psi(W, x)$ which comes out of (2) as a by-product, Born has shown that its square may be satisfactorily interpreted as giving the probability that the particle lies between x and $x+dx$ when it is in the state of energy W. This is really the ground for requiring that ψ remain finite. For an energy level, such that $\psi(W, x)$, does not remain finite as $x\to\pm\infty$, the probability that it is not "at infinity" is vanishingly small, and therefore these states do not exist physically. Adopting the probability interpretation of $\psi(W, x)$ one has at once the result that there is a finite probability of being outside the range of the classical motion of that energy.

[3] Born, Zeits. f. Physik **38**, 806 (1926).

[4] Heisenberg, Zeits. f. Physik **43**, 172 (1927); Bohr, Nature, April 14, 1928.

A simple case is the lowest state of the harmonic oscillator, which has the energy $h\nu/2$. The $\psi(W, x)$ for this state is $e^{-1/2(x/a)^2}$ so $\psi^2 = e^{-(x/a)^2}$ where a is the classical amplitude of motion associated with this energy. The probability of being outside the classical range is therefore

$$\frac{2\int_a^\infty e^{-(x/a)^2}dx}{\int_{-\infty}^{+\infty} e^{-(x/a)^2}dx} = 0.157$$

or more than 15 percent.

When one studies the behavior of $\psi(W, x)$ from (2) for a $V(x)$ somewhat like the one in Fig. 1, he finds that, if the W is one for which ψ is finite everywhere, then ψ approaches zero very rapidly (exponential decrease) as $x \to \pm\infty$. In the neighborhood in which $W - V(x)$ is small, the function takes on appreciable values and has oscillatory character where $W - V(x) < 0$, and non-oscillatory character elsewhere. Cases like that of Fig. 1 have been discussed by Hund[6] in connection with his studies of molecular spectra.

An important case is that in which the potential energy curve consists of a single "obstacle" or barrier as in Fig. 2, and the motion is one of insufficient energy, W, to clear the obstacle. In such cases there are *two* finite solutions $\psi_1(W, x)$, and $\psi_2(W, x)$ associated with each energy level, W, and so an arbitrary linear combination of them is also a solution of (2). Born has shown that there is always a combination of them which depends on x as e^{+ikx} and represents a pure left-to-right progressive wave motion as $x \to +\infty$. Such a solution for x large and negative can then be said to represent an incident left-to-right wave coming from the left side and a reflected wave which is not as strong as the incident wave. The interpretation is that the incident beam of particles is partly reflected and partly transmitted. In the range where $(W - V) < 0$ the de Broglie wave-length h/p becomes imaginary, and so gives rise to an exponential behavior of ψ whose nearest analogue is, perhaps, in optics in the slight penetration of a refracted ray into a rarer medium even beyond the angle of total reflection where the refracted angle is imaginary. In this way, one can find the probability that a particle coming up from the left will get through the wall and escape to the right. The case illustrated in Fig. 3a for which

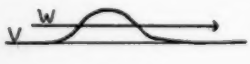

Fig. 2.

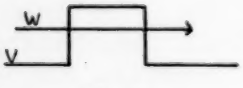

Fig. 3a.

$$V(x) = 0 \qquad x < -a,$$
$$V(x) = V \qquad -a < x < 0,$$
$$V(x) = 0 \qquad x > 0,$$

and for $0 < W < V$, is a simple one with which to illustrate the nature of the calculation. For a given energy level, W, there are two ψ functions satisfying

[6] Hund, Zeits. f. Physik 40, 742 (1927); Wentzel, Zeits. f. Physik 38, 518 (1926).

the requirements of finiteness everywhere and of continuity for the ordinates and slopes at the discontinuities in $V(x)$.

These are readily found to be

$$\psi_1(W,x)=\begin{cases}\cosh\sigma_2 a\cdot\cos\sigma_1(x+a)-(\sigma_2/\sigma_1)\sinh\sigma_2 a\sin\sigma_1(x+a) & (x<-a)\\ \cosh\sigma_2 x & (-a<x<0)\\ \cos\sigma_1 x & (0<x)\end{cases}$$

$$\psi_2(W,x)=\begin{cases}-(\sigma_1/\sigma_2)\sinh\sigma_2 a\cdot\cos\sigma_1(x+a)+\cosh\sigma_2 a\sin\sigma_1(x+a) & (x<-a)\\ (\sigma_1/\sigma_2)\sinh\sigma_2 x & (-a<x<0)\\ \sin\sigma_1 x & (0<x)\end{cases} \tag{3}$$

where $\sigma_1=(2\pi/h)(2\mu W)^{1/2}$ and $\sigma_2=(2\pi/h)[2\mu(V-W)]^{1/2}$. To find the ψ function corresponding to a beam of particles incident from the left which is partly transmitted and partly reflected, one has to add these together in such a way that to the right of the obstacle there is only the pure left-to-right flow, i.e., one must take

$$\psi_1(W,x)+i\psi_2(W,x)$$

To the left of the obstacle, the ψ function represents the superposition of a left-to-right, or incident beam

$$\left.\psi_{inc}=\left[\cosh\sigma_2 a-\frac{i}{2}\left(\frac{\sigma_1}{\sigma_2}-\frac{\sigma_2}{\sigma_1}\right)\cdot\sinh\sigma_2 a\right]e^{i\sigma_1(x+a)}\right\}\quad x<-a \tag{4}$$

and a reflected beam

$$\left.\psi_{ref}=\frac{i}{2}\left(\frac{\sigma_1}{\sigma_2}+\frac{\sigma_2}{\sigma_1}\right)\sinh\sigma_2 a e^{-i\sigma_1(x+a)}\right\}$$

The transmitted beam is simply

$$\psi_{tr}=e^{i\sigma_1 x}\qquad x>0 \tag{5}$$

These expressions have, of course, the conservation property

$$(\psi\bar{\psi})_{inc}=(\psi\bar{\psi})_{ref}+(\psi\bar{\psi})_{tr}.$$

The probability that a particle coming up to the wall shall get through to the other side is simply $(\psi\bar{\psi})_{tr}\div(\psi\bar{\psi})_{inc}$ which for $e^{\sigma_2 a}\gg 1$ is clearly equal to

$$P_a(W)=16(W/V)(1-W/V)e^{-2\sigma_2 a}. \tag{6}$$

The controlling factor is the exponential term except when W/V is very near to 0 or 1.

For application to a theory of the pulling of electrons out of metals by electric fields Fowler and Nordheim[6] have derived the probability expression by similar methods for the curve of Fig. 3b, i.e.

$$V(x)=0\qquad x<0$$
$$V(x)=C-Fx\qquad x>0$$

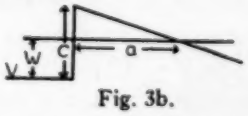

Fig. 3b.

[6] Fowler and Nordheim, Proc. Roy. Soc. **A119**, 1 (1928).

The probability that a particle of energy W get through the wall they find to be

$$P_b(W)=4[(W/C)(1-W/C)]^{1/2}\exp(-4k(C-W)^{3/2}/3F)$$

from their Eq. (18) p. 178. The term in the exponent can be written

$$4k(C-W)^{3/2}/3F=4\sigma_2/3a \quad (k^2=8\pi^2\mu/h^2) \tag{7}$$

to exhibit the similarity with the case of the square wall. Here a is the positive value of x for which $V(x)=W$, and σ_2 is defined as

$$\sigma_2=(2\pi/h)[2\mu(C-W)]^{1/2}.$$

The exponents in each of these cases can be written in the form

$$(4\pi/h)\int[2\mu(V-W)^{1/2}dx$$

the integration extending across the barrier, the limits being the two places where $V(x)-W=0$.

Application of the method of approximate integration of Schrödinger's wave equation which was first used in quantum mechanics by Wentzel[5] indicates that such a result is quite general. The probability of getting through the wall at a single approach is governed essentially by the factor

$$\exp\left\{-(4\pi/h)\int[2\mu(V-W)]^{1/2}dx\right\} \tag{8}$$

being equal to it except for a factor of the order of magnitude of unity.

We have next to consider the case of a potential energy curve of the type shown in Fig. 4. According to classical mechanics there are two modes of motion associated with energy levels below the maximum such as W in the figure. One is a periodic motion in the range I while the other is an aperiodic motion in the range II. By the Bohr-Sommerfeld rule the periodic motions would give a discrete spectrum of allowed energy levels which would overlie the continuous spectrum associated with the aperiodic motions. On the quantum mechanics every energy level is allowed with the essential difference that *there are no energy levels with which two types of motion are associated*. With each energy level there is associated just one wave function $\psi(W, x)$ whose square gives the relative probability of being at different parts of the possible range of x. The $\psi(W, x)$ functions do show traces of the discreteness of the energy levels which the Bohr-Sommerfeld rule associates with the perodic motions in I, in an interesting way. The $\psi(W, x)$ for every W show sinusoidal oscillations as $x\to\infty$ and also oscillate in the range I. For most energies the amplitude of the oscillations in the range II is overwhelmingly large compared to that in range I, the ratio being of the order of $\exp\{(2\pi/h)\int[2\mu(V-W)]^{1/2}dx\}$ the integration extending across the barrier. This situation is just reversed however for little ranges of W values near those given by the old quantization rules. For these the amplitude in I is large compared to that in II in the same ratio. These then are the "allowed"

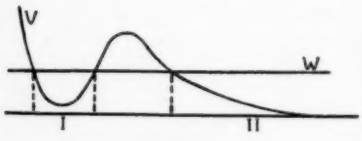

Fig. 4.

energy levels. It is not a stationary state for the particle to be in range I and remain there. But for certain energy levels there is an extraordinarily large probability of being in unit length of range I relative to unit length of range II.

We have to find the mean time which a particle remains in the range I before "leaking through" to the outer range II. This can be obtained from the following simple consideration. When the particle is at a place of x large and positive, $V(x)=0$ (Fig. 4) so the energy is all kinetic and the speed is therefore $(2W/\mu)^{1/2}$. The amount of time which the particle spends in unit length for x large is therefore $(\mu/2W)^{1/2}$. The time spent in a range of length a is therefore $a\ (\mu/2W)^{1/2}$. Now according to the wave-functions the probability of being in unit length of range I for one of the quasi-discrete energy values relative to the probability of being in unit length of range II is of the order $\exp\{(4\pi/h)\int[2\mu(V-W)]^{1/2}dx\}$. Therefore since the motion is aperiodic and the particle escaping from range I will in the mean only go through unit length of II once, the time T which must be spent in range I before getting through to range II is of the order of

$$T\sim a(\mu/2W)^{1/2}\exp\left\{(4\pi/h)\int[2\mu(V-W)]^{1/2}dx\right\}$$

where a is of the order of the breadth of range I.

Like all of the results of quantum mechanics this is to be interpreted as a probability result. So that if we start with a number of particles in the same allowed energy level in identical regions similar to range I, the number which leak out in time dt is governed by

$$dN=-N\lambda dt$$

which gives the usual exponential law of decay $N(t)=N_0e^{-\lambda t}$ where

$$\lambda=1/T. \tag{9}$$

The expression for T may be arrived at in a somewhat different way. One can think of the particle as executing its classical motion in range I, but as having at each approach to the barrier the probability of escaping to range II given by expression (8) above. The frequency of the periodic motion in I, which represents the number of approaches to the barrier in unit time, is of the order $a(\mu/2W)^{1/2}$ so the mean time of remaining in range I before excape comes out as the quotient of these two quantities as before. The reader will find it of interest to examine Oppenheimer's formula[7] for the pulling of electrons out of hydrogen atoms by an electric field. His formula for the mean time required for dissociation of the atom by a steady electric field splits naturally into a factor which is the classical frequency of motion in the Bohr orbit multiplied by an exponential probability factor of the type of expression (8) used in this paper.

2. Application to Radioactive Disintegration

After the exponential law in radioactive decay had been discovered in 1902, it soon became clear that the time of disintegration of an atom was

[7] Oppenheimer, Proc. Nat. Acad. Sci. **14**, 363 (1928).

as independent of the previous history of the atom as it was of its physical condition. One could not for example suppose that an atom at its birth begins to lose energy by radiation and that its instability is the result of the drain of energy from the nucleus. On such a view it would be expected that the rate of decay would increase with the age of the atoms. When later it was observed that the number of atoms breaking up per second showed the fluctuations demanded by the laws of probability it became clear that the disintegrating depended solely on chance. This has been very puzzling so long as we have accepted a dynamics by which the behaviour of particles is definitely fixed by the conditions. We have had to consider the disintegration as due to the extraordinary conjunction of scores of independent events in the orbital motions of nuclear particles. Now, however, we throw the whole responsibility on to the laws of quantum mechanics, recognizing that the behaviour of particles everywhere is equally governed by probability.

From what was said in the preceding section it is clear that the property of the nucleus which we need to know in order to apply the theory is its potential energy curve; and this happens to be a property which we know fairly definitely. Outside a nucleus whose net charge is given by the atomic number we should expect to find a Coulomb inverse-square field of the appro-

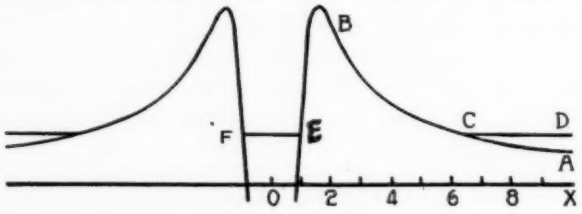

Fig. 5. The unit of abscissas is 10^{-12} cm. The horizontal line gives the energy of the α-particle emitted by uranium, 6.5×10^{-6} ergs.

priate strength. And it is well known that in experiments on the scattering of alpha particles from heavy nuclei the proper inverse-square field is found to extend through the whole accessible region. In Fig. 5 the curve AB is a plot of the potential energy of an alpha particle in this field against the distance from the centre of a nucleus of atomic number $Z=90$. To provide the attractive field which holds alpha particles in the nucleus it has long been recognized that the potential energy curve must turn over in the way shown in Fig. 5. And it has been shown, for example by Enskog,[8] that curves of this type may be obtained by giving the particle a magnetic moment.

In order to explain the ejection of a particle one has hitherto supposed that the praticle in the internal region received energy sufficient to raise it over the potential barrier. The suggestion that this energy was obtained by absorption of some ultra-penetrating radiation from outside never received wide acceptance. But it was necessary on classical mechanics to suppose that the emitted particle had received energy, if not from outside then from the other nuclear particles. Now the potential barrier which confines particles in the nucleus, i.e. the area under the curve in Fig. 5, is a region where

[8] Enskog, Zeits. f. Physik 45, 852 (1927).

the total energy would be less than the potential energy. And since the quantum mechanics endows particles with the new property of being able to penetrate such regions, this gives us at last a nucleus which can disintegrate without the absorption of energy.

We see that a mere qualitative application of the principles of quantum mechanics seems to account for the principal properties of radioactive atoms, most of which have been familiar for nearly thirty years. We have now to consider the question: How can nearly similar nuclei have periods of decay of anything from a small fraction of a second to over 10^9 years? It has been shown above that in coupling the possible motions of a particle on either side of a potential barrier, the probability of transmission through the barrier is extremely sensitive to the area of the barrier; in fact the relation to it is exponential. In this way we shall show that we can obtain all rates of decay up to practical stability, and that from atoms whose potential curves are almost identical.

3. Quantitative Application

If the height of *CD* above *OX* in Fig. 5 gives the energy of the alpha-particle emitted, we have to consider the coupling of the motion along *CD* with the motion along *EF* inside the nucleus. We clearly do not have much choice in the area of the potential barrier we may take, since both the point *C* is fixed and the curve passing through *C*. For the purposes of numerical calculation we will compare radium A which has a period of 4.4 minutes (half-value period 3.05 minutes) with the extreme cases of uranium and

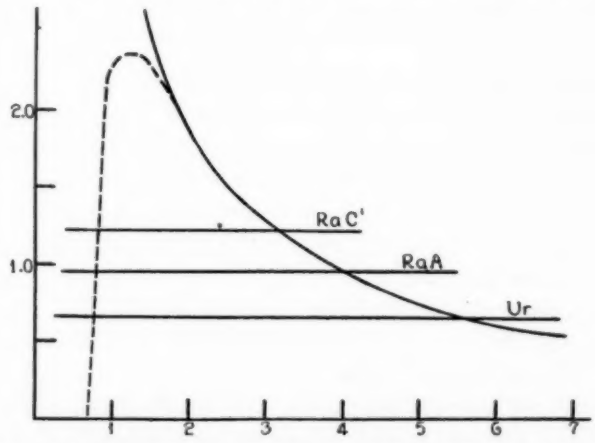

Fig. 6. The unit of ordinates is 10^{-6} ergs, and the unit of abscissas 10^{-13} cm.

radium C′, which have decay periods of about six thousand million years and a millionth of a second respectively.

An alpha-particle emitted by an element of atomic number Z escapes through the Coulomb field corresponding to $(Z\text{-}2)$. Hence the potential energy for $Z=82$, which has been plotted in Fig. 6 is appropriate to radium A. The three horizontal lines in Fig. 6 give the energies of the alpha-particles

[9] Blackett, Proc. Roy. Soc. **A107**, 369 (1925).

from Ra A, Ra C′, and Uranium, which are 1.22×10^{-5}, 9.55×10^{-6}, and 6.5×10^{-6} ergs respectively. It is clear that the factor $(V\text{-}W)$, which occurs in the expression (9), given above for the rate of decay, is simply the vertical distance between the horizontal line for W and the potential energy curve for the proper value of Z-2. In Fig. 7 is plotted a curve derived from Fig. 6 giving the value of $(4\pi/h)\ [2\mu(V-W)]^{1/2}$ for Ra A as a function of the radius. The upper curve is for uranium and the lower for Ra C′, derived from curves for the proper atomic numbers.

From these curves we can at once find how large a barrier we have to take in order to obtain any observed rate of decay. For the integral occurring in the exponent of expression (9) is merely the area that we will take under the curve in Fig. 7. Since the unit of abscissas taken is 10^{-12} cm and the unit of ordinates 10^{13} cm^{-1}, each of the squares in Fig. 7 has the dimensionless value 10; so that for an element whose potential barrier has an area of one

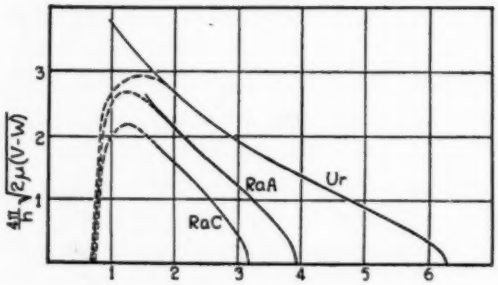

Fig. 7. Ordinates give the value of $(4\pi/h)[2\mu(V-W)]^{1/2}$ the unit being 10^{13} cm^{-1}. The unit of abscissas is 10^{-12} cm.

square on this diagram we should employ the factor e^{-10}. The broken line in Fig. 6 has been drawn so as to give for Ra A in Fig. 7 an area of approximately the value 53.7. For substituting this value in expression (9) together with $W=9.55\times10^{-6}$ and $a=10^{-12}$ we obtain the decay constant $8.45\times10^{20}\times e^{-53.7}=3.8\times10^{-3}$ sec.$^{-1}$, or the decay period $1/\lambda$ is 4.4 minutes in agreement with observation. In the expression for λ the precise value of the first factor is obviously unimportant, for if it were taken five times larger or smaller this would only alter the area of the required barrier by about 1 percent. The general size of the potential barrier in Fig. 6 that we have had to take seems to be a very reasonable one.

Now we reach an unexpected result. In drawing the areas for uranium and Ra C′ in Fig. 7 the continuous lines were predetermined, and the broken lines have been derived from the curve in Fig. 6, already used for Ra A. The values of the two areas are found to be 34.4 and 90, though the exact values depend on how the broken line is made to join the Coulomb potential curves. On substituting the values 34.4 and 90 in the expression for T we obtain for Ra C′ and uranium decay periods of the order of 10^{-6} sec. and 10^{10} years respectively, in agreement with observation.

It was already clear from Fig. 6 that we should obtain for all elements some qualitative agreement with the Geiger-Nuttall relation: the higher

the energy of the alpha-particle the greater the rapidity of decay. But now we have found the unexpected result that the agreement is almost quantitative; that we do not have to choose a different potential energy inside the nucleus for each alpha-particle but having taken one potential curve for the whole series, it is the energy of the emitted alpha-particle which determines its own rate of decay. The mere fact that the velocity of the alpha-particle from Ra A, 1.69×10^{9} cm per sec. is a little greater than the 1.4×10^{9} cm per sec. of uranium, and a little less than the 1.92×10^{9} cm per sec. of Ra C′, gives Ra A a decay period 10^{15} times as short as that of uranium and 10^{8} times as long as that of Ra C′, in agreement with observation. Questions raised by this agreement with the factor of Geiger and Nuttall will be discussed in the last section of this paper. The radius 2×10^{-12} cm, at which we have taken the deviation from the inverse-square law, seems to be of the magnitude which our knowledge of the nucleus would lead us to expect.

Further we see at once why it is that no slow alpha-particles have been discovered. Although particles of ranges between 2.5 and 7 cm are plentifully distributed, no alpha-particles of energy less than 6.5×10^{-6} ergs have been found. But we now see from Figs. 6 and 7 that for particles of lower energy the area of the potential barrier increases very rapidly; so that for particles of range 2 cm or less the exponential factor would reduce the rate of decay of the element to a value at which its manifestation of radioactivity would be beyond the limits of detection.

Beta-ray disintegration.—It has been customary to assign the central core of the nucleus as the habitat of the nuclear electrons, with a potential energy curve of the type shown in Fig. 8. The outer slope AB again represents the Coulomb inverse-square field, as in Fig. 5. But since the charge of the electron is $-e$ instead of $+2e$ the potential energy is reversed in sign, and of half the magnitude of that in Fig. 5. There is nothing new in this assumed curve, although it looks somewhat artificial; this type of curve for the nuclear electron was obtained for example by Enskog in the paper referred to above.[8] What is new is the suggestion that an electron in the internal region again has a certain chance of penetrating the barrier, and of escaping at any time along CD with kinetic energy given by the height of CD above the axis.

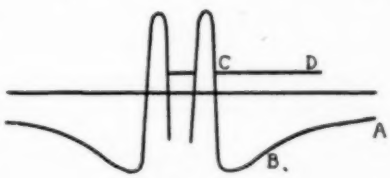

Fig. 8.

If we have alpha and beta-particles both with this chance of escaping from the nucleus, it might be thought that every radioactive element should be found to disintegrate part with expulsion of alpha-particles and part with beta-particles. But we would repeat that the chance of escape is extremely sensitive to the height to which the potential energy curve rises above the energy-level in question; and that if the size of this potential barrier be increased by a small factor the probability of escape may be decreased more than a million-fold. There seems then no reason why there should not be

the three types of disintegration: that in which the probability of escape is much greater for an alpha-particle than for an electron; that in which it is much greater for an electron than for an alpha-particle; and that in which the probabilities of escape are comparable. The last gives the branching type of disintegration as shown by Ra C, of which 99.97 percent emits beta-particles, and 0.03 percent alpha-particles. By taking this view of the disintegration process, we have raised the question: Does any radioactive element have a unique mode of disintegration, or does it merely appear unique in most cases because the secondary mode is a million times less frequent and escapes detection? The present discussion certainly favours the latter alternative. It need not surprise us then that so few cases of branching disintegration have so far been discovered, since it is unlikely (so far as we know) that the areas of the potential barriers will in many nuclei happen to have just that relative size which will give for alpha and beta-particles comparable probabilities of escape.

Artificial disintegration.—Blackett's cloud-chamber photographs[9] of artificial disintegration in nitrogen showed that the impinging alpha-particle was caught and retained by the nucleus. One is tempted to apply the present theory, using again the fact that the impinging alpha-particle may penetrate the barrier of potential, this time from the outside, instead of passing over the top as required by classical theory. But when we do this we are at once confronted by the fact that instead of approaching the barrier 10^{20} times per second, like a nuclear particle, our alpha-particles will only make one impact apiece. So it would seem that the capture of the alpha-particle could not be due to penetration. There is, however, another consideration; and that is that if the impinging alpha-particle have an energy very near that of an allowed but unoccupied nuclear energy-level, the chance of its penetrating the barrier at a single impact approaches unity. This property has already been referred to in section 1.

4. Experimental Evidence for the Penetration of Potential Barriers

The essential basis of the present theory is the assumed power of particles to pass through regions where their total energy would by classical mechanics be less than their total energy. For this property there is no direct experimental evidence in physics, although it follows from the laws of quantum mechanics. But in applying this to the nucleus we have found that we can actually *obtain* direct experimental evidence. Though on classical mechanics the passage of a particle through such a forbidden region was a manifest absurdity, it was found in 1925 by Rutherford and Chadwick[10] that that is exactly what the alpha-particles from uranium appear to do.

Consider the alpha-particle which the uranium nucleus emits during its disintegration. The alpha-particle will gain energy in escaping through the repulsive Coulomb field outside the nucleus. This energy is given on classical theory as $2Ze^2/r$. Even if the alpha-particle leaves its place in the nucleus

[10] Rutherford and Chadwick, Phil. Mag. **50**, 889 (1925).

with no initial velocity, its energy cannot be less than this amount. The energy with which the alpha-particles leave the disintegrating Uranium atom is observed experimentally to be 6.5×10^{-6} ergs. On referring to Fig. 5, which was drawn for $Z=90$, we see that this energy corresponds to $r=6.3\times10^{-12}$ cm and if any of the energy was initial energy and not acquired through falling through the repulsive field, the value of r would have to be greater than this value.

It was concluded that the inverse-square law of repulsive field could not possibly hold within this value of r. Consequently if we fire at the uranium nucleus an alpha-particle having slightly more energy than the $6.5\ 10^{-6}$ ergs, it should penetrate its structure to where the Coulomb law no longer holds; while still faster particles should penetrate, even when not fired directly at the nucleus. It was therefore disconcerting when, on examining the scattering of fast alpha-particles fired at uranium, Rutherford and Chadwick could find no indication of any departure from the inverse-square laws. The Coulomb field was found to hold inside the radius from which the uranium alpha-particle appeared to come. That is to say, the uranium alpha-particle appeared to emerge from a region where its kinetic energy was negative. To escape this conclusion Rutherford[11] supposed that the uranium alpha-particles before ejection are electrically neutral, having been neutralised by two electrons which they leave behind when they are ejected. This hypothesis succeeded in circumventing the paradox. But if we abandon classical mechanics, the paradox disappears, yielding us direct experimental evidence in favor of the phenomenon of quantum mechanics in which we are interested.

5. Discussion of Limitations

It must be clearly understood that although the Coulomb part of the potential curve outside the nucleus, represented by AB in Fig. 5 is necessarily common to all particles, the internal part is merely intended to represent the potential energy of a particular alpha-particle. And it must not be taken to represent a general central field common to many particles, such as we are so accustomed to in atomic structure. There is no reason why the internal field should be necessarily symmetrical about the center of the nucleus as drawn in Figs. 5 and 8. In fact, Rutherford[12] has suggested that the nucleus may have something analogous to a crystalline structure. If this caution is lost sight of, difficulties are encountered.

For the atom of each radioactive element contains within its nucleus not only the alpha-particle which it will itself emit, but also the alpha-particles destined to be emitted by its successors in the radioactive series. Now if the velocity of escape of the alpha-particles from each element were always less than that of those emitted by its predecessors, there would be no serious difficulty; for from an atom loaded with alpha-particles in various allowed energy levels, the particle in the highest level would have the

[11] Rutherford, Phil. Mag. **4**, 580 (1927); Proc. Phys. Soc. **39**, 370 (1927).
[12] Rutherford, Jour. Franklin Inst. **198**, 743 (1924).

greatest probability of escape. This however is the opposite of what is observed; and we have to account for the subsequent emission of particles of higher energy than that emitted by the parent substance. We may do this by supposing either (a) that the alpha-particles of higher energy have in the parent element been confined by correspondingly high barriers; or (b) by supposing that the alpha-particles in the nucleus are not permanently in the high energy levels from which they emerge, but are temporarily raised up from lower levels. The latter seems to be a retrograde step, for the principle advantage of the present theory is that it has offered an escape from such processes.

If, however, we accept the former supposition (a), we see that the emission of one alpha-particle must profoundly modify the potential barrier which confines the alpha-particle destined to be emitted next. As we have shown, the Geiger-Nuttall relation seems to require that the barrier through which this alpha-particle emerges be approximately the same in all elements of the series. But until we know how this comes about, it seems inadvisable to discuss the Geiger-Nuttall relation in greater detail. In speaking of the energy of one particle in the nucleus, it must not be forgotten that we are making use of the simplification mentioned in the introduction: that of discussing one nuclear constituent alone.

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PRINCETON UNIVERSITY,
November 20, 1928.

REFLECTION OF SOFT X-RAYS

By S. D. Gehman

Abstract

Reflecting power of Al, C and Pt for non-characteristic soft x-rays (40–500 volts) as function of angle and voltage.—Non-characteristic soft x-rays of voltage range 40 to 500 were passed through a slit system and then reflected from the polished surfaces of various mirrors in a high vacuum. The reflecting power of the mirror was measured by a photoelectric method, as a function of the voltage for a given angle of incidence and as a function of the angle for a given voltage. The reflecting power::voltage curve for aluminum, angle of beam and mirror 13°, shows a broad maximum between 68 and 140 volts and falls off rapidly as the voltage increases. The same curve for carbon, angle 14°, has a similar maximum between 250 and 350 volts. For a platinum mirror, same angle, the curve rises for voltages up to about 100 and then the reflecting power decreases very slowly for higher voltages. The reflecting-power:: angle-of-incidence curve shows a rapid decrease of the reflecting power as the angle of incidence decreases; its form appears to be practically independent of the voltage for the range used. The results appear to justify the conclusion that for aluminum and carbon, light elements, the reflecting-power::plate-voltage curve shows a maximum related to a critical potential but the resolving power of the method, as here used is inadequate to locate these potentials with useful precision.

Introduction

HOLWECK'S work with non-characteristic soft x-rays showed that they could be reflected by a metal mirror.[1] The purpose of this research was to investigate the way in which the reflecting power of a metal mirror varied for wave-lengths including some of its own critical wave-lengths, in the hope that this would serve as a new method for locating the critical wave-lengths of the atoms of the mirror.

The intensity distribution among the various wave-lengths which appear in the continuous spectrum of soft x-rays generated by electron bombardment has been discussed by Holweck.[2] The shortest wave-length obtained is given by the quantum relation, $\lambda_0 = 12345/V$ in which V is the plate voltage and λ_0 is the shortest wave-length in Angstrom units. A decided maximum of the x-ray energy, however, occurs for a longer wave-length given by $\lambda_m = 1.3\lambda_0$.[3] λ_m is then the effective wave-length corresponding to a voltage V, and this relation makes possible the study of the reflecting power of a metal mirror as a function of the wave-length of the incident radiation for these long waves.

Apparatus

The experimental tube used in this work is shown diagrammatically in Fig. 1. It was made of Pyrex and was evacuated by means of two mercury diffusion pumps. Two traps immersed in liquid air protected the tube from

[1] Holweck, De La Lumière aux Rayons X, p. 83.
[2] Reference 1, p. 43.
[3] Reference 1, p. 44; Compton, X-rays and Electrons, p. 48.

mercury vapor. The pressure during operation, as indicated by a McLeod gauge, was of the order of 10^{-6} mm of mercury.

In Fig. 1, the element A is the cathode and anti-cathode. The anti-cathode consisted of a piece of sheet molybdenum carried by two vertical rods fastened in lavite blocks at the top and bottom. The cathode was a tungsten filament stretched a millimeter or so in front of the anti-cathode and fastened in stubs carried by the lavite blocks. The x-rays passed through two slits, 1 mm wide, in diaphragms 5 cm apart in the copper cylinder B. C and C' are lavite bushings which supported grids D, E, F, protecting the photo-electric target T, from any stray ions. This target was molybdenum and was connected to a Compton tilted-needle electrometer used at a sensitivity of 2000 divisions per volt. Grid D was usually grounded, E was kept at -90

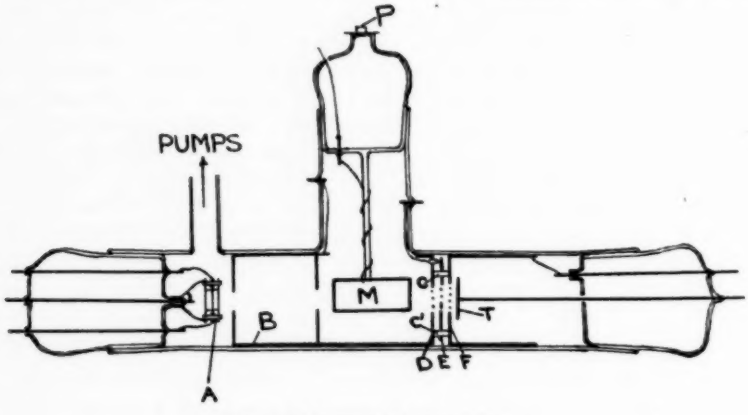

Fig. 1. Diagram of apparatus.

and F at $+90$ volts. The mirror M was carried by a holder attached to a glass tube on the bottom of the central stopper. The aluminum mirror was a piece of polished aluminum; the platinum mirror was sputtered on plate glass; the carbon mirror was a piece of polished mineral graphite.

A small silvered prism P was mounted on the top of the central stopper and the deflections of a beam of light reflected from its face on a scale 3.4 meters away served to determine the angles turned through by the mirror.

Method

The mirror was adjusted by means of a beam of visible light before the end stoppers were put in the tube. It was set parallel to the line of the slits but just outside the beam so that it was necessary to turn the mirror through a small angle before it began to intercept the beam.

The ratio of the photoelectric current obtained when the mirror intercepted the beam to that when the mirror was set parallel to the beam, measured the reflecting power of the mirror.

Results

The curves in Fig. 2 show how the reflecting power of the aluminum mirror varied with the angle between the beam and the mirror, for a given plate voltage. Similar curves were obtained for other voltages. The apparent rapid

decrease at the start is due to the fact that the mirror has not yet intercepted the whole beam. With the wider slits, curve B, it is necessary to turn through

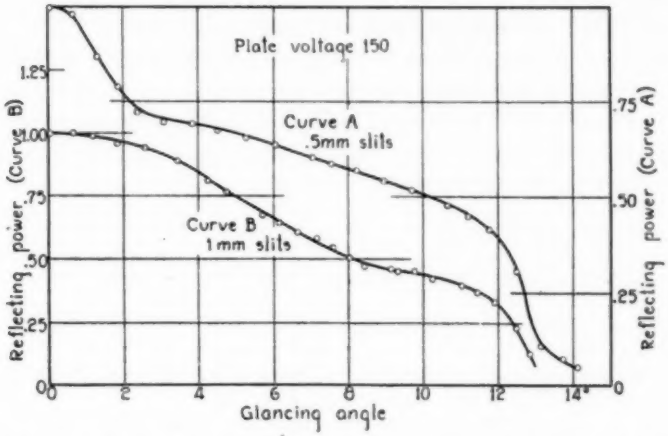

Fig. 2. Curves showing the reflecting power of an aluminum mirror as a function of the angle between the x-ray beam and mirror.

a larger angle before the mirror cuts the entire beam. Consequently only those portions of the curves beyond the first bend represent the variation of the reflecting power with the angle.

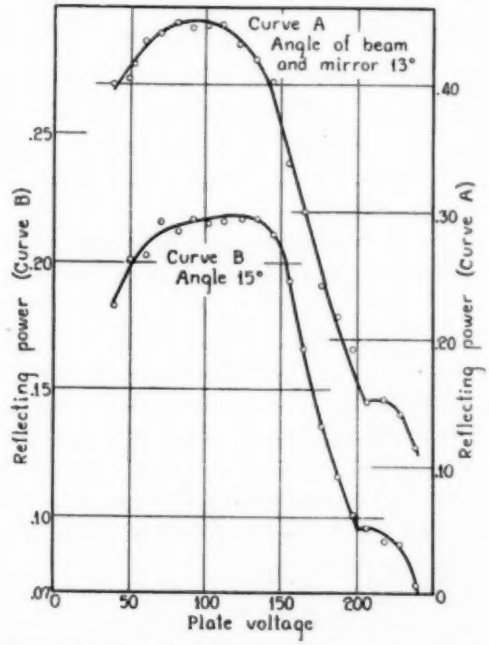

Fig. 3. Curves showing the reflecting power of an aluminum mirror as a function of the voltage generating the x-rays.

Fig. 3 gives curves showing how the reflecting power of aluminum varied as a function of the plate voltage, the angle being fixed. The $L_{II,III}$ levels of

aluminum have been located by a number of observers at 68 volts.[4] The maximum in the curves in Fig. 3 might be connected with this level. It is to be remembered that it would be necessary to run the voltage up to 96 volts before the effective wave-length corresponds to 68 volts.

The L_I level of aluminum has been located at 123 volts.[5] The plate voltage necessary to produce effective radiation corresponding to this voltage would be 160. It is possible that the irregularity at the bottom of the curves is connected with this critical level but if so, it is so badly displaced that very little significance can be attached to it.

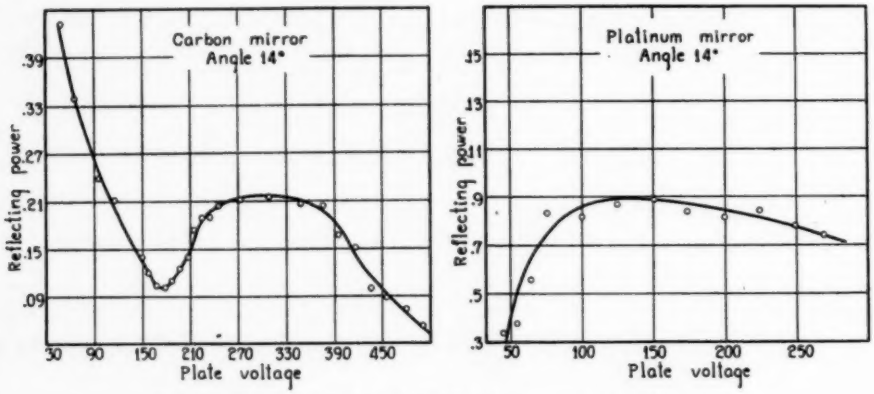

Fig. 4. Curves showing the reflecting power of carbon and platinum as a function of the x-ray voltage.

The curve for carbon, which is given in Fig. 4 shows the same broad type of maximum as occurred for aluminum, and its position is related in about the same way to a critical potential. The $K\alpha$ line for carbon is at 272 volts[6] and the K absorption limit is 12 volts higher.[7] The maximum in the curve lies between 250 and 350 volts.

In the case of platinum, the curve has a different character and does not show a definite maximum. Perhaps this is due to the superposition of many critical potentials.

The maxima at the critical potentials of the mirrors are suggestive of the way in which materials reflect at their absorption bands in the infra-red.

The results appear to justify the conclusion that for aluminum and carbon, light elements, the reflecting power-plate voltage curve shows a maximum related to a critical potential but the resolving power of the method, as here used, is inadequate to locate these potentials with useful precision.

This work was done under the direction of Dr. Bazzoni to whom I am also indebted for suggesting the problem.

UNIVERSITY OF PENNSYLVANIA,
October 15, 1928.

[4] Holweck, De La Lumière aux Rayons X, p. 131.
[5] Kurth, Phys. Rev. **18**, 470 (1921).
[6] Weatherby, Phys. Rev. **32**, 707 (1928).
[7] Thibaud, Phys. Zeits. **29**, 241 (1928).

ARC SPECTRUM OF NITROGEN IN THE EXTREME ULTRA-VIOLET

By K. T. Compton and J. C. Boyce

Abstract

Analysis and classification of lines in the arc spectrum of nitrogen.—Excitation of nitrogen by controlled electron impact was found to bring out many lines in the arc spectrum of nitrogen. These were observed with a vacuum spectrograph in the region from 500 to 1200A. The lines thus found, together with material of Hopfield, Bowen, and Fowler in the extreme ultra-violet, and of Merton and Pilley in the visible, and the multiplets already found by Kiess have led to a fairly complete analysis of the spectrum, in good agreement with the predictions of the Hund theory. The *ionization potential* is 14.48 volts, and the metastable levels ^2D and ^2P have energies corresponding to 2.37 and 3.56 volts respectively, in good agreement with the predictions of Kaplan and Cario from a study of active nitrogen.

THE analysis of the arc spectrum of nitrogen is rendered peculiarly difficult by several circumstances. Arc types of excitation tend to bring out principally the strong band systems which, in the far ultra-violet, may look like a system of lines and may mask arc lines. More strenuous excitation brings out spark lines. Most of the arc lines are in regions inconveniently far in the infra-red or the ultra-violet. Spectra obtained by Merton and Pilley[1] under peculiar conditions of excitation and by Kiess[2] in the near infra-red enabled the latter author to work out the skeleton of the spectral structure involved in the near-visible region, comprising eight quartet and five doublet multiple levels. The quartet levels were specified with reference to the ionization limit, but the doublet levels were given only relative values, since no series were found.

In an abstract of a paper before the American Physical Society, Hopfield[3] announced the discovery of two doublet and two quartet series in the extreme ultra-violet and gave the formula for one of these series. He has recently very kindly furnished us with prints of the lantern slides which he showed at that time. Hopfield connected one quartet and one doublet series with the higher terms found by Kiess (although the following analysis shows the latter of these connections to be only partially correct and at least two of his series to involve misgrouping of lines).

We have photographed in our vacuum spectrograph the extreme ultra-violet spectrum of nitrogen excited by single electron impacts at voltages between 20 and 100 volts and have been able to work out the general structure of the entire nitrogen arc spectrum. Several details in this scheme are admittedly uncertain and provisional, but there can be little doubt about the correctness of the general structure, in view of the resemblance to the known

[1] Merton and Pilley, Proc. Roy. Soc. **A107**, 411 (1925).
[2] Kiess, Jour. Opt. Soc. Am. **11**, 1 (1925).
[3] Hopfield, Phys. Rev. **27**, 801 (1926).

structure of O II and of the possibilities allowed by the Hund theory. There is particular interest attached to certain features of this analysis in relation to the peculiarities of "active" nitrogen.

Fig. 1 is a Grotrian diagram of the nitrogen atom. The Hund theory predicts five ground states: the lowest state $2p^4S_2$ and the four metastable ground states $2p^2D_{3,2}$ and $2p^2P_{2,1}$. Going to the $^3P_{3,2,1}$ limit are series of

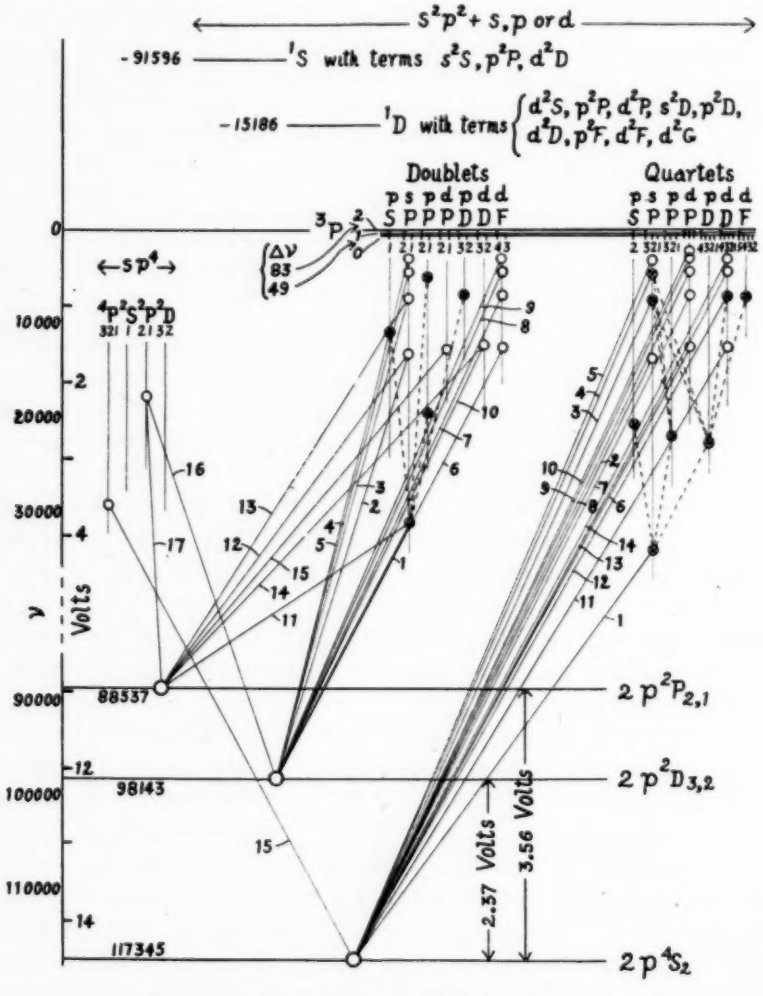

Fig. 1. Grotrian diagram of the nitrogen atom.

quartet and doublet terms. Other series of doublet terms go to the higher ^1D and ^1S limits. The normal electron configuration of the outer shell of electrons is s^2p^3. The foregoing excited states arise from the displacements of one of the p electrons. A less common mode of excitation involves the displacement of an s electron, for which the most significant terms are the four shown in the upper left corner of Fig. 1. The solid disks are the terms previously identified by Kiess, and the broken diagonal lines show the combi-

nations on which his identification was based. The solid diagonal numbered lines are the ultra-violet combinations thus far identified.

TABLE I. *Identified terms*

(**Bowen[4])	Quartets		(*Kiess[3])	Doublets	
$2p^4S_2$	117345		$2p^3D_{2,3}$	98143	
			$2p^3P_{1,2}$	88537	
$3s^4P_1$	34059*		$3s^2P_1$	31239*	
P_2	34026*	34	P_2	31156*	83
P_3	33979*	47	$4s^2P_1$	13240	
$4s^4P_1$	13724		P_2	13157	83
P_2	13674	50	$5s^2P_1$	7340	
P_3	13606	68	P_2	7264	76
$5s^4P_1$	7532*		$6s^2P_2$	4554	
P_2	7487*	44	$7s^2P_2$	3183	
P_3	7417*	70			
$6s^4P_1$	4779*		$3p^2P_1$	19607*	
P_2	4734*	45	P_2	19571*	36
P_3	4662*	72	$5p^2P_1$	5082*	
$7s^4P_2$	3211 ±		P_2	5056*	26
$3p^4S_2$	20593*				
			$4p^2S_1$	10898*	
$3p^4P_1$	21868*	18			
P_2	21850*	38	$4p^2D_2$	6855*	
P_3	21812*		D_3	6832*	23
$3p^4D_1$	22573*				
D_2	22550*	23	$3d^2P_1$	12728	
D_3	22513*	37	P_2	12771	−43
D_4	22462*	51			
			$3d^2D_2$	12247	
$3d^4P_1$	12481				
P_2	12455	26	$3d^2F_3$	12557	
P_3	12388	117	F_4	12486	71
$4d^4P_1$	7022		$4d^2F_3$	7066	
P_2	6994	28	F_4	7004	62
P_3	6946	48	$5d^2F_4$	4472	
$5d^4P_2$	4471		$6d^2F_4$	3096	
P_3	4436	35		Terms from sp_4	
$6d^4P_2$	3068		$sp^4\ ^2P_1$	17671	
$7d^4P_2$	2242		P_2	17701	−30
$3d^4D_2$	12523		$sp^{44}P_1$	29176**	−18
$4d^4D_1$	7069*		P_2	29194**	−44
D_2	7124*	−54	P_3	29238**	
D_3	7057*	66			
D_4	6942*	115			
$5d^4D_2$	4520				
$6d^4D_2$	3157				
$4d^4F_2$	7159*				
F_3	7131*	18			
F_4	7097*	35			
F_5	7041*	56			

Table I gives the values of the terms shown in Fig. 1. Kiess' values are given for his quartet terms, and also for his doublet terms except for a bodily shift from his arbitrary scale to a new scale determined from the computed series limits. The remaining terms are determined from a consideration of all the data at present available in the extreme ultra-violet region.

[4] Bowen, Phys. Rev. **29**, 231 (1927).

TABLE II. *Quartets from* $2p^4S_2 = A$

No.	Combination	Calculated	Observed		Hopfield[5]		Note
1	$A-3s^4P_1$	83286	83283	6	83286	3	a
	P_2	83319	83318	7	83320	4	
	P_3	83366	83369	7	83366	5	
2	$A-4s^4P_1$	103621	103619	2	103739	1	
	P_2	103671	103673	3	103669	2	
	P_3	103739	103742	4	103736	3	
3	$A-5s^4P_1$	109813	109818	0	109813	1	
	P_2	109858	109865	1	109856	2	
	P_3	109928	109926	2	109926	2	
4	$A-6s^4P_1$	112566			112562	0	
	P_2	112611			112609	0	
	P_3	112683	112672	0	112680	1	
5	$A-7s^4P_3$	114140 ±	114140 ±	00			
6	$A-3d^4P_1$	104864	104878	2	104864	1−	
	P_2	104890			104890	1	b
	P_3	105007	105010	2	105003	3	
7	$A-4d^4P_1$	110323	110307	3*d*	110323	0	b
	P_2	110351			110351	1	c
	P_3	110399	110401	3*d*	110396	3	
8	$A-5d^4P_2$	112874	?		112874	0	
	P_3	112909	112908	1	112910	2	b
9	$A-6d^4P_3$	114277	114277	0.5			b
10	$A-7d^4P_3$	115103	115103	00			b
11	$A-3d^4D_3$	104822	104822	3	104823	1	
12	$A-4d^4D_1$	110276					
	D_2	110221					
	D_3	110288	110307	3*d*	110296	0	c
13	$A-5d^4D_3$	112825	112830	0.5	112821	1	
14	$A-6d^4D_3$	114188	114188	0			d
15	$A-sp^4\,{}^4P_1$	88169	88160	3	88185	2	e
	P_2	88151			88167	4	
	P_3	88107	88107	3	88123	6	

TABLE III. *Doublets from* $2p^2D_{2,1} = B$

No.	Combination	Calculated	Observed		Hopfield		Note
1	$B-3s^2P_1$	66904	66900 B	2	66908	4	
	P_2	66987	66987 B	2	66996	6	f
2	$B-4s^2P_1$	84903	84906	2	84919	1	
	P_2	84986	84984	2.5	85005	2	g
3	$B-5s^2P_1$	90803	90798	00	90811	0	
	P_2	90879	90879	1	90883	0	
4	$B-6s^2P_2$	93589	93589	0.5			
5	$B-7s^2P_2$	94960	94960	00			
6	$B-3d^2F_3$	85586	85575	2	85589	3	h
	F_4	85657	85646	2	85666	4	
7	$B-4d^2F_3$	91077	91086	0	91073	0	
	F_4	91139	91134	2	91144	1	
8	$B-5d^2F_4$	93671	93671	1			
9	$B-6d^2F_4$	95047	95047	00			
10	$B-3d^2D_3$						
	D_3	86896	85903	0*d*			i
16	$B-sp^4\,{}^2P_1$	80466	80472 F	4			
	P_2	80436	80442 F	7			j

[5] Hopfield (from unpublished data referred to in Ref. 3; also Hopfield and Liefson, Astrophys. J. **58**, 59 (1923).

TABLE IV. *Doublets from* $2p^3P_{1,2}=C$

No.	Combination	Calculated	Observed		Hopfield		Note
11	$C-3s^5P_1$	57298	57298 B	3	57296	8	
	P_2	57381	57381 B	3	57379	10	k
12	$C-4s^5P_1$	75297	75301 F	1			
	P_2	75380	75377 F	2			
13	$C-5s^5P_1$	81197					
	P_2	81273	81321 F	4*d*			l
14	$C-3d^5D_3$						
	D_3	76290	76283 F	5*d*			
15	$C-3d^5P_1$	75809	75809 F	2			
	P_2	75766	75766 F	5			m
17	$C-sp^{4\,5}P_1$	70860					
	P_2	70830	70822 F	4	70827	2	n

Tables II, III and IV summarize the facts upon which the analysis is based.

NOTES ON TABLES

(a) These three lines are among the extreme ultra-violet standards determined by Bowen and Ingram,[6] whose measurements, together with Kiess' s^4P term values, were used to fix the value of the $2p^4S_2$ ground term.

(b) Hopfield's photographs, taken in the second order, resolve P_1 and P_2, which are just too close for us to separate. The reasons for identifying this and Nos. 7–10 as d^4P combinations are as follows. Kiess identified the $4d^4D$ and $4d^4F$ terms, and the s^4P terms are all accounted for. The only remaining terms on the Hund scheme, which could combine with the ground A state are of the type d^4P. The series Nos. 6–10 is therefore, by exclusion, ascribed to these terms. This is supported by the fact that such combinations should be stronger than those with d^4D or d^4F, and because, by analogy with O II, the d^4P terms should be higher than d^4D or d^4F, as is found to be the case in comparing with Kiess' $4d^4D$ and $4d^4F$ terms. Also the progressively smaller interval as we go to higher members indicates a d^4P series. The terms are not, however, inverted as in O II.

(c) The combinations of A with Kiess' terms $4d^4D_{1,2,3}$ give predicted lines at 110276, 110221, 110288 respectively. Our apparatus would probably not resolve the first and last of these from the $P_{1,2}$ lines. Hence probably all four lines are blended in our diffuse line 110307. We did not definitely find the other predicted lines 110186 and 110214 from Kiess' $4d^4F_{2,3}$ terms although there was a faint diffuse band very near this. Such ^4S with ^4F combinations would, however, be expected to be quite weak.

(d) An additional support of the classification of the series A, md^4P and A, md^4D is the fact that the strongest lines in each (associated with the P_3 and D_3 terms) have about the expected frequency separation 83 characteristic of the fact that d^4P_3 terms go to $^3P_2$ and d^4D_3 terms go to $^3P_1$ as limits.

(e) These $^4P_{1,2,3}$ levels were fixed from the values given by Bowen and Ingram as wave-length standards, and the identification of the term was first made by Bowen.[4]

[6] Bowen and Ingram, Phys. Rev. **28**, 444 (1926).

(f) These lines lie beyond the range of our spectrograph. The lines marked "B" are from Bowen and Millikan.[7] For theoretical reasons elaborated later in the paper, we should expect that the experimental frequency separation in each doublet of this type should be 4 or 5 units too large. That this is so is a strong support of this phase of the analysis. This remark applies to lines 1–5 and 6–9. The discrepancy should be less in case of line 10.

(g) Here the discrepancy between our measurements and Hopfield's is quite large. However our values check well with a combination with Fowler's lines shown in lines 12 Table IV. Probably such discrepancies as these fall within limits of error of plate calibrations except in the case of lines measured with precision in higher orders.

(h) In O II these combinations are next in strength to those of $B-ms^2P_{1,2}$ and the d^2F levels are midway between the d^2D and the d^2P levels. The assignment here given makes this also true for N I.

(i) In O II the d^2D levels are higher and have smaller separation than either the d^2P or the d^2F levels. This suggests that this unresolved line is due to the assigned combination. Furthermore, the $3d^2P$ level (an inverted one) is already fixed by Kiess, and we find its combination in Table IV. We should expect the $B-d^2P$ combination to be the weakest of the three d doublet sets, and it is not surprising that we find it to be the missing one.

(j) These $sp^4\ ^2P_{1,2}$ levels are fixed by analogy with O II, as having about the expected position and separation and as being inverted as shown by the intensities. F means that these lines were measured by Fowler and Freeman,[8] who listed them as probaly arc lines. We also found these lines strongly but unresolved. They came so near the edge of our plate, however, that our measurement of them is not accurate.

(k) These lines as well as the corresponding $B-3s^2P_{1,2}$, show reversal in some of Hopfield's photographs. B signifies that we have used Bowen's measurements in this region which our plates do not cover. Lines 12–15 show Fowler's measurements. (15) is calculated from Kiess' term value and shows excellent agreement. In the 13 and 17 the agreement is not so good, but there are certain reasons for this as follows:

(l) The observed value is some 50 wave-numbers larger than the calculated values, the line is diffuse and stronger than would be expected in view of the intensities of the two preceding members of the series. However the observed diffuse line must include the $C-4d^2P_{1,2}$ lines whose exact wave-numbers cannot be calculated since the term $4d^2P_{1,2}$ is not known. By comparing with the combinations of C with the $3d$ terms we should expect $C-4d^2P_{1,2}$ to lie at about 81350 and to be stronger than $C-5s^2P_{1,2}$. Consequently the observed diffuse line lies just in the midst of these four expected lines. Our resolving power should suffice to separate them. Our intensity was so low, however, that we could barely see something in this region but could not measure or resolve it, and hence we can only use Fowler's value.

[7] Bowen and Millikan, Phil. Mag. **48**, 259 (1924).

[8] Fowler and Freeman, Proc. Roy. Soc. **A114**, 662 (1927).

Fowler states that his diffuse line is probably a group of several lines, and he is uncertain as to their arc or spark character.

(m) Classed by Fowler as probably arc lines. The correspondingly predicted combination of B with these d^2P levels was not observed, but would be expected to be relatively weak.

(n) Comparing with note (j) it is seen that, if the present identification is correct, there must be a relative error of about 14 wave-numbers between Fowler's measurements of 80442 (1243) and 70822 (1412). Also we should expect a weaker companion of 1412, which has not been reported. Fowler judges 70822 to be a spark line from its behavior, but has not fitted it into his spark classification.

Discussion

The metastable states. These are identified through connecting them with the $3s^2P_{1,2}$ states by the lines 1492, 1495 and 1742, 1745 which are the first members of two series of doublets converging to the $^3P_{0,1,2}$ limit. Hopfield correctly evaluated the latter series, although he could not correctly "label" it because his work antedated the Hund classification. The entire set of relations here has, however, remained in doubt for a reason which is actually a strong support of the classification. Consider the expected relations as shown by Fig. 2.

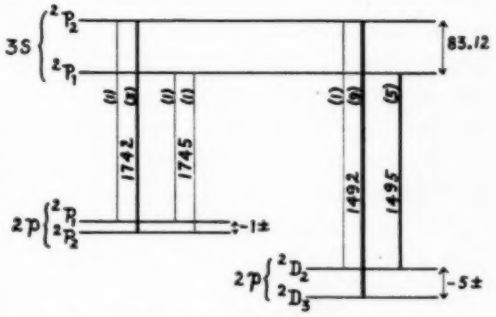

Fig. 2. Term diagram for nitrogen atom.

The upper P_1P_2 separation of 83.12 is known from the near visible lines analyzed by Kiess. The separations of the two lower pair of terms can be estimated approximately from analogy with O II, where the lower P_1P_2 separation is -4.5 and that of D_2D_3 is -19.8. We should therefore expect the corresponding separations in N I to be approximately -1 and -5 respectively, as shown in Fig. 2.

No spectrograph has yet been used, in this region of the spectrum, which could resolve lines as close as 1 or even 5 wave-numbers. Consequently the four predicted lines of the $2p^2P_{1,2}-3s^2P_{1,2}$ combination would appear as two lines, of relative intensities 2 and 1, and with a separation almost exactly 83.12. The $2p^2D_{2,3}-3s^2P_{1,2}$ combination of three lines would appear as two, of intensity ratio 2 to 1, but with separation about 5 units greater than 83.12. This is exactly what is found:

1742.740		1492.83	
57380.9		66986.9	
1745.260	82.8	1494.78	87.4
57298.1		66899.5	

Thus the argument which has been used against connecting both the 1742 and the 1492 pairs to the $3s^2P_{1,2}$ levels is, in the light of the predictions of the

Hund theory and of analogy with O II, really a convincing evidence of this connection. Similar considerations apply to the higher series combinations with these low levels.

Further evidence for this assignment of terms is found by applying the irregular doublet law. Knowing the low terms in O II to be ^4S 283028, ^2D 256200, ^2P 242558, and in N I the term ^4S 117345, we predict the other low N I terms ^2D 99983 and ^2P 91748. These are each within two or three percent of the values calculated from the strong 1742 and 1492 pairs, and there are no other lines in their vicinity.

Finally the fact that some of Hopfield's photographs show the 1492 and 1742 pairs in absorption would seem to complete the proof of this assignment. But there is still the following evidence.

Active nitrogen. Work in this laboratory by Kaplan and Cario,[9] on which a preliminary note has appeared in Nature, appears to give the complete explanation of this long-puzzling substance. Active nitrogen contains metastable molecules in the ^3S state[10] of energy about 8.2 volts and also metastable atoms of energies about 2.4 and 3.7 volts. The afterglow arises from excitation of the metastable molecules by the metastable atoms. The metastable molecules may be removed and the afterglow extinguished by passing the gas through a highly heated tube, but the 2.4 and 3.7 volt metastables are shown to persist and, beyond the heated region, to replenish the supply of metastable molecules by recombination,—thereby renewing the afterglow.

By investigating the intensities of spectra of various substances when excited by active nitrogen, Kaplan and Cario fixed the energies of the metastable atoms certainly within a few tenths of a volt of the values 2.37 and 3.56 given by the present analysis.

Accuracy of the series limits. For the series $A-ms^4P_3$ the quantum defects run regularly $3s$ 1.20, $4s$ 1.16, $5s$ 1.15, $6s$ 1.15, $7s$ 1.16±, and the calculated limit is about 117350. For the series $A-md^4P_3$ the quantum defects are more irregular: $3d$ 0.02, $4d$ 0.03, $5d$ 0.03, $6d$ 0.02, $7d$ 0.01 and the limit is calculated as about 117361. Hopfield calculated 117353, and Kiess 117345. We have arbitrarily used Kiess' limit as the one to which to refer our quartet terms. It appears, however, that a value about 8 or 10 units larger might be more accurate. Hopfield has already given the ionization potential as 14.48 volts.

For the doublet series, $B-ms^2P_2$ gives quantum defects; $3s$ 1.12, $4s$ 1.11, $5s$ 1.11, $6s$ 1.10, $7s$1.13, and the estimated limit is about 98150. For the series $B-md^4F_4$ the quantum defects are very regular, $3d$ 0.03, $4d$ 0.04, $5d$ 0.05, $6d$ 0.06 with the estimated series limit 98143, which is probably the most accurate of the four.

These considerations show that the absolute scale of term values is probably accurate within about 10 units. No inter-system combinations between the doublet and quartet terms have been found (nor in O II), so that a direct tying together of the two systems is impossible. Consequently inter-system

[9] Kaplan and Cario, Nature **121**, 906 (1928); also more detailed article soon to appear in Zeits. f. Physik.

[10] Sponer, Zeits f. Physik **34**, 622 (1925); Birge and Hopfield, Astrophys. J. (in print).

combinations are less accurately predicted from Table I than are intra-system combinations.

Spark lines. Bowen[4] has identified a number of N II lines in the extreme ultra-violet. Of these, 18 lie between the extremes 533 and 1085, and therefore within the range of our plates (which took in the region 0–1250). We find all Bowen's lines, and with very satisfactory agreement in wave-lengths and intensities (except that we could not resolve several of his closest groups), except for one striking omission: we failed entirely to excite his strong group 644.633, 644.836, 645.180. Furthermore we have not succeeded in exciting spectra higher than the first spark in any gas thus far tried, i.e., N, Ne, A,[11] although we have gone to voltages well above those which should, energetically, be necessary. Consequently we have come to the provisional conclusion that single electron impacts do not disturb more than two electrons in an atom,—at least in the range of moderate energies. However this may be, the results indicate that Bowen's group 644–645 is due to some special condition of excitation of N II not present in our discharge. Fowler[12] has recently come to the same conclusion on other grounds, for he does not list this group but, instead, assigns weak lines near 776 to the combination suggested for 644–645 by Bowen. We find this line on our plates.

In conclusion we may say that the essential parts of the structure here proposed for N I seem to us to rest on quite convincing evidence, but the details in analyzing some close lines where no check in the near visible region is possible may require revision. We are at present experimenting with a novel type of discharge, with which we hope to discover some of the faint lines predicted by this analysis but not yet found.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.,
November 9, 1928.

[11] Compton, Boyce, and Russel, Phys. Rev. **32**, 179 (1928).
[12] Fowler, Proc. Roy. Soc. **A118**, 44 (1928).

THE EXCITATION OF THE AURORA GREEN LINE IN ACTIVE NITROGEN

By Joseph Kaplan

Abstract

The aurora green line has been excited in the nitrogen afterglow when oxygen was present in the discharge in which the active nitrogen was produced and observed. The interpretation of this phenomenon is based on the recent hypothesis as to the nature of active nitrogen as presented by Kaplan and Cario.

LAST spring the writer[1] reported the excitation of the aurora green line in active nitrogen. In view of the developments since then in the study of active nitrogen it is now thought that a more detailed discussion of the above experiment would be of some value. It is the purpose of this paper therefore to discuss the excitation of the green oxygen line in active nitrogen.

The apparatus used was very simple. The discharge tube was a 500 cc Pyrex bulb through which a condensed discharge from a 1-kw., 15000-volt Thordarsen transformer was passed. The gas was pumped through the discharge tube continuously at a pressure of about 0.5 mm. The spectrum of the afterglow was photographed on a small Hilger spectrograph for the visible and the glow in the discharge tube was photographed by using a rotating sectored disk which was adjusted so as to allow only the light of the afterglow itself to fall on the slit of the spectrograph. Eastman Astronomical Green plates were used. The dispersion was necessarily very small and for that reason the accuracy of the wave-length determination was only about

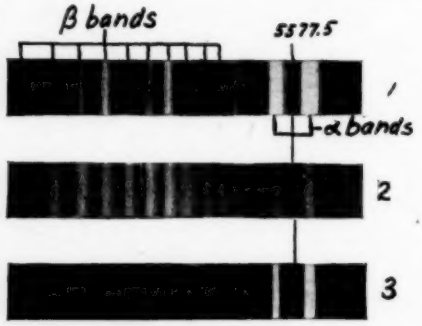

Fig. 1. (1) Afterglow in 4% O_2, 96%N_2, exposure, 12 hours; (2) afterglow in 20% O_2, 80% N_2, exposure 12 hours; (3) afterglow in commercial N_2, exposure, 12 hours.

0.1A. The wave-length found for the green line was 5577.5 instead of the very accurate value of 5577.35A found by Babcock.[2] The experimental conditions under which the line appeared however are such as clearly to show that

[1] Kaplan, Nature **121**, 711 (1928).
[2] Babcock, Astrophys. J. **57**, 209 (1923).

the line was caused by the presence of the oxygen and it is obvious therefore that the conclusion as to its identity is correct.

The three spectra show clearly the conditions under which the line was excited. In spectrum 1 the percentage of oxygen was about 3 or 4 percent and the β bands of NO are fairly well developed. The green line is more intense on this plate than some of the β bands and also much more intense than the weaker α bands. In spectrum 2 the percentage of oxygen is about 20 and the green line is weak, much weaker in fact than most of the β bands. The α bands are also extremely weak. In spectrum 3 the α bands are very strong, the green line is extremely faint and the β bands are very faint. The percentage of oxygen in this case was very small, commercial nitrogen having been used.

It is possible from these three spectra and from evidence as to the nature of active nitrogen, to draw a clear cut interpretation as to the method by which the excitation of the green line took place.

According to the recent views of Cario and the author,[3] the spectrum of active nitrogen can best be explained if it is assumed that in addition to normal atoms there are present metastable molecules in the A level and metastable atoms in the ^2D and ^2P levels. The energy of the metastable atoms in the ^2P state is 3.56 volts and that in the ^2D level is 2.37 volts.[4] In order that the α bands be strongly developed in the afterglow it is essential that these metastable atoms be present in the glow in great numbers. On spectrum 1, on which the α-bands are very strong and the green line also strong, these conditions are fulfilled. There are present metastable atoms and undoubtedly atomic oxygen that has been formed in the discharge itself. Collisions between metastable atoms of nitrogen in the ^2P state and normal oxygen atoms give rise to the excitation of the green line. That the energy of 3.56 volts is more than enough to do this is shown in the discussion of the aurora spectrum by the author.[5] In this it is pointed out that the difference between $^1S_0$ and ^3P cannot be greater than 3.4 volts. The ^2D metastable atoms can raise the atom from the $^1D_2$ state to the $^1S_0$ state, which is now thought to be the upper level of the green line transition.[6] It is interesting here to point out that the green line can be observed with appreciable intensity in a discharge only when argon is mixed with the oxygen. The explanation of this can readily lie as Cario suggested,[7] in the frequency of transitions in argon which lie between 2.9 and 3.1 volts. From the discussion of the auroral spectrum it is possible to show that the difference $^1S_0 - {}^3P$ is roughly about equal to 3.0 volts and this indicates that argon is effective in exciting atomic oxygen by collisions of the second kind in which 2.9 to 3.1 volt transfers are effective. On spectrum 2, the green line is only feebly developed in spite of the presence of 20 percent oxygen. At the same time the α-bands were very weak showing

[3] Cario and Kaplan, Nature **121**, 906 (1928).
[4] Compton and Boyce, Phys. Rev. **33**, 145 (1928).
[5] Kaplan, Proc. Nat. Acad. Sci., in press.
[6] McLennan, McLeod and Ruedy, Phil. Mag. **6**, 558 (1928).
[7] Cario, Journal Franklin Inst. **205**, 575 (1928).

that the number of metastable nitrogen atoms was very small and consequently that the green line excitation could be only feeble, in spite of the presence of considerable oxygen. This agrees with the interpretation suggested above.

In spectrum 3 there is almost no excitation of the green line because of the presence of only a very small amount of oxygen. This plate simply gives added proof that the line is due to oxygen. It is significant that the green line was excited only when the afterglow was photographed in the discharge tube itself. Cario was unable in only a few attempts to observe the line in active nitrogen that had diffused away from the discharge in which it had been formed. The failure to observe the green line away from the discharge can readily be explained if it is remembered that atomic oxygen combines very readily with molecular oxygen to form ozone. The absence of the green line outside of the discharge can be ascribed to the absence of atomic oxygen outside of the discharge itself. This indicates that the collisions which are essential in the excitation of the green line are probably the ones discussed here. There is enough energy available in metastable molecules of nitrogen and in three body collisions with atoms or in collisions with excited molecules to dissociate the oxygen molecule into atoms. Apparently this process does not occur readily since it is well known that the mixing of oxygen with active nitrogen results in the formation of nitric oxide and the excitation of NO bands. A detailed discussion of this point however requires more experimental facts and will not be attempted here. The experimental work discussed in this paper was done while the author was a National Research Fellow at Princeton University.

UNIVERSITY OF CALIFORNIA AT LOS ANGELES,
November 27, 1928.

RELATIONS BETWEEN DOUBLETS OF STRIPPED ATOMS IN FIVE PERIODS OF THE PERIODIC TABLE

By R. C. Gibbs and H. E. White

Abstract

Principal and diffuse doublets of stripped atoms in five periods of the periodic table from Li I to O VI, Na I to Cl VII, K I to Mn VII, Rb I to Zr IV, and Cs I to Pr V. —Combining the data now available for the one-electron systems of the second, third, fourth, fifth and sixth periods certain regularities are found to exist between the successive elements in each period and between corresponding elements in successive periods. These regularities are found by the application of the regular and irregular doublet laws. For the long periods which involve more penetrating orbits extrapolations of Z_4 and s_4 (Landé's formula) prove to be better guides in identifying doublets of the higher members of a sequence although extrapolation of s (Sommerfeld's formula) is entirely satisfactory for the sequences in the short periods. Using the former we have been led to correct our previous identifications of the principal doublet of Ce IV. The tighter binding of the d electron over both the s and p electrons starting with Sc III, Yt III, and La III in the three long periods is especially well brought out by the Moseley type of diagram. Evidence is presented to indicate that the unexcited state of Ce IV involves a $5d$ rather than a $4f$ electron. New data are given for V V, Cr VI and La III.

WHEN all of the orbital electrons of an atom of an element, in excess of those possessed by an atom of the rare gas next preceding it in the periodic table, are removed, such an atom is said to be "stripped" of its outer shell of electrons. Emission lines resulting from transitions between energy levels that arise from the return of the first of these "stripped" off electrons are often referred to as spectra of one-electron systems. In such a system the energy levels always have a doublet character. To distinguish from the spectra of lower states of ionization these spectra of one-electron systems are designated, for example, in the third period as Na I, Mg II, Al III, etc.

Paschen[1] and Fowler[2] identified many lines in the spectra of sodium, magnesium, aluminum, and silicon as belonging to the various series for one-electron systems of these elements. Landé[3] was the first to point out the similarity between the first doublet of the principal series of these elements and the regular doublets of the x-ray spectra. This correlation between x-ray spectra and optical spectra led him to the correct assignment of the various k's and j's of the x-ray levels K_{I}, $L_{\text{I,II,III}}$, $M_{\text{I,II,III,IV,V}}$, etc. Assuming that the selection principle holds for the intra-atomic x-ray levels as well as it does for the optical spectra of the alkalies and the alkaline earths, de Broglie and Dauvillier[4] pointed out that the $L_{\text{II}}L_{\text{III}}$ doublet is analogous to the p doublet of the alkalies, and that they therefore have the same azimuthal

[1] Paschen, Ann. d. Physik **71**, 142 (1923).
[2] Fowler, Proc. Roy. Soc. **A103**, 413 (1923); Phil. Trans. Roy. Soc. **225**, 1 (1925).
[3] Landé, Zeits. f. Physik **16**, 394 (1923).
[4] de Broglie and Dauvillier, Jour. d. Physique et le Radium, [VI] **5**, 1 (1924).

quantum number. Bowen and Millikan[5] have shown that not only the regular doublet (relativity doublet) law but also the irregular doublet law may be applied to the one-electron systems of the second and third periods. With the aid of these laws they have been able to identify lines in "hot-spark" spectra of one-electron systems from Li I to O VI and from Na I to Cl VII. By applying these same doublet laws to the one-electron systems in the fourth fifth and sixth periods starting with K I and Ca II, Rb I and Sr II, and Cs I and Ba II we have been able[6] to identify the first pair of lines of the principal series for elements as far as Mn VII, Zr IV and Pr V, and also certain lines belonging to the diffuse series.

The values of $(\Delta\nu/\text{const.})^{1/4}$ and of s (*screening constant*) given in columns 3 and 4 of Table I have been determined by Bowen and Millikan and the authors from Sommerfeld's formula for regular doublets.[7]

For the sake of comparison we have computed values of Z_i and s_i columns 5 and 6 of Table I, from Landé's formula for penetrating orbits,[8]

$$\Delta\nu=\frac{R\alpha^2(Z-s_a)^2(Z-s_i)^2}{n^3k(k-1)}=\frac{R\alpha^2Z_a^2Z_i^2}{n^3k(k-1)}.$$

Although it is doubtful what physical significance can be attached to these quantities, (s, Z_i, and s_i), they served admirably as guides in predicting approximately the principal doublet separations and together with the irregular doublet law made it possible to identify with certainty the lines belonging to these doublets.

For the less penetrating orbits of the short periods the extrapolations from values of s were entirely satisfactory, although it is evident that nearly, if not equally, as satisfactory results might have been obtained by extrapolating from values of Z_i or s_i. However, for the more penetrating orbits, as for example in the sixth period, the latter extrapolation is a more reliable guide. The value of s as previously reported by us[6] for Ce IV showed no irregularity in the progression of this screening constant for the caesium-like sequence, and consequently we felt that our identifications for the Ce IV doublet were correct. Recently in computing the values of Z_i it was suspected that the frequency separation of this doublet was not large enough as the curve for Z_i for this sequence exhibited a marked change in slope between La III and Ce IV. Since we had selected these lines from data given by Exner and Haschek and by Eder and Valenta for the spark spectrum of cerium, photographs were taken in this laboratory using a high-voltage spark between graphite electrodes cored with cerium nitrate. Plates taken in this way reveal a large number of lines nearly all of which belong to the first and second spark spectrum. There are, however, on the plates, which cover a range of about

[5] Bowen and Millikan, Phys. Rev. **24**, 209 (1924); **25**, 295 (1925); **26**, 150 (1925); **27**, 144 (1926).

[6] Gibbs and White, Proc. Nat. Acad. of Sci. **12**, 448, 551, 588, 675 (1926); Phys. Rev. **29**, 359 (1926).

[7] Sommerfeld, Atombau, 4th German Ed. p. 420.

[8] Landé, Zeits. f. Physik **25**, 48 (1924).

600A, two lines appearing to have come only from the tips of each electrode, ($\lambda_{vac}=2779.07$ and $\lambda_{vac}=2457.59$) that stand out from all the rest. This type of *short line*, as is well known, is characteristic of high states of ionization. Hence we conclude that these two lines, constitute the $6^2S_1-6^2P_{1,2}$ doublet of Ce IV. Neither of these lines is listed by Exner and Haschek or by Eder and Valenta. The frequency separation, as thus definitely identified, yields a value of 56.05 for Z_i which is much more consistent with those of the preceding elements of this sequence, than 55.52 obtained from our previous identifications. See Table I.

TABLE I. *Regular doublet law.*

Atom		$\Delta\nu$	$(\Delta\nu/\text{const})^{1/4}$	s	Z_i	s_i
			Second period ($2^2P_1-2^2P_2$)			
Li	I	0.338	0.981	2.02	0.93	2.07
Be	II	6.61	2.06	1.94	2.06	1.94
B	III	34.4	3.12	1.88	3.14	1.86
C	IV	107.4	4.14	1.86	4.18	1.82
N	V	259.1	5.16	1.84	5.21	1.79
O	VI	533.8	6.18	1.82	6.24	1.76
			Third period ($3^2P_1-3^2P_2$)			
Na	I	17.18	3.55	7.45	7.66	3.34
Mg	II	91.55	5.39	6.61	9.56	2.44
Al	III	234.0	6.82	6.18	10.91	2.09
Si	IV	461.8	8.08	5.92	12.08	1.92
P	V	794.8	9.26	5.74	13.15	1.85
S	VI	1267.1	10.40	5.60	14.23	1.77
Cl	VII	1889.5	11.50	5.50	15.29	1.71
			Fourth period ($4^2P_1-4^2P_2$)			
K	I	57.7	5.96	13.04	14.85	4.15
Ca	II	222.8	8.36	11.64	17.24	2.76
Sc	III	474.3	10.09	10.91	18.29	2.71
Ti	IV	817.5	11.57	10.43	18.99	3.01
V	V	1264.7	12.91	10.09	19.54	3.46
Cr	VI	1821.5	14.15	9.85	19.98	4.02
Mn	VII	2464.7	15.25	9.75	20.19	4.81
			Fifth period ($5^2P_1-5^2P_2$)			
Rb	I	237.60	10.04	26.96	31.23	5.77
Sr	II	801.46	13.60	24.40	34.81	3.19
Yt	III	1553.7	16.05	22.95	36.29	2.71
Zr	IV	2484.9	18.05	21.95	37.10	2.90
			Sixth period ($6^2P_1-6^2P_2$)			
Cs	I	554.0	14.23	40.77	49.55	5.45
Ba	II	1690.9	18.81	37.19	53.88	2.12
La	III	3095.7	21.76	35.24	55.52	1.48
Ce	IV	4707.0	24.30	33.70	56.05	1.95

The line previously selected by us[6] for Pr V at $\lambda=2295.4$, listed by Exner and Haschek as a spark line of praseodymium, is in all probability a carbon line. We have taken several photographs, using first graphite and then tin electrodes cored with praseodymium oxalate and with praseodymium chloride, but with unsatisfactory results. The lines we have measured for the principal doublet are very weak and rather uncertain and therefore they have not been included in the tables.

How closely the irregular doublet law (i.e. the linear progression of frequency with atomic number for transitions involving no change in total quantum number) is followed, is shown in Fig. 1 for all five periods. It is therefore possible to use the irregular doublet law to predict the approximate wave-numbers, i.e. the location in the spectrum, for succeeding elements in any sequence.

In computing term values Bowen and Millikan utilized the hydrogenic nature of circular orbits, a procedure which in general is suitable for the lighter elements. In the long periods, however, we have used a method sug-

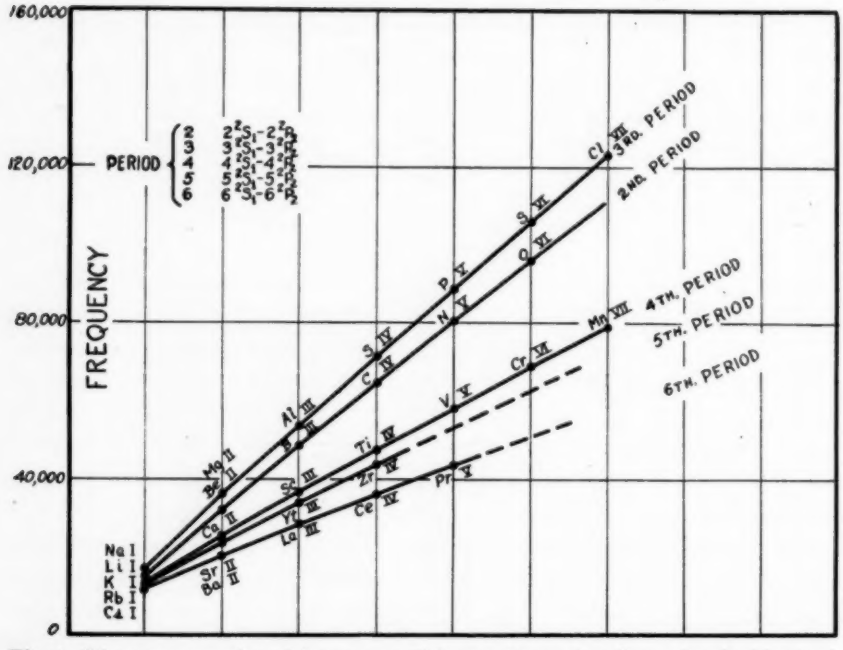

Fig. 1. Linear progression of frequency with atomic number (irregular doublet law).

gested by Hartree[9] for penetrating orbits which yields results that are fairly accurate. Term values computed in this way differ very little from those obtained by the ordinary methods that can be applied when several members of a series are known.

From Fig. 2 it may be seen that term values of any sequence when plotted on a Moseley diagram show very nearly a straight line relation. A consequence of the irregular doublet law is that $\Delta(\nu/R)^{1/2}$ for any sequence should be independent of atomic number. As shown in Fig. 2 this relation is especially well followed for the *S-P* levels in all five periods. Although there is a marked change in the initial slope of the $^2D_3$ lines between the third and fourth periods there is a gradual increase in the downward curvature of the line itself in going from one period to the next. The $^2F_4$ lines also show this increase in curvature in going from one sequence to the next but instead of

[9] Hartree, Roy. Soc. Proc. **A106**, 552 (1924).

curving downward, as do all the other lines, they curve upward. This indicates that in the sixth period the 4^2F_4 line will eventually cross the 5^2D_3 line even though in going from Cs I to Ba II they diverge from each other. If the term values of the $4^2F_{3,4}$ levels, given by Paschen and Götze, are correct for Ba II then we should expect that these F and D lines would not cross before Ce IV is reached, and that therefore the first electron bound to the stripped atom of cerium is a *5d* electron. This appears to be in contradiction

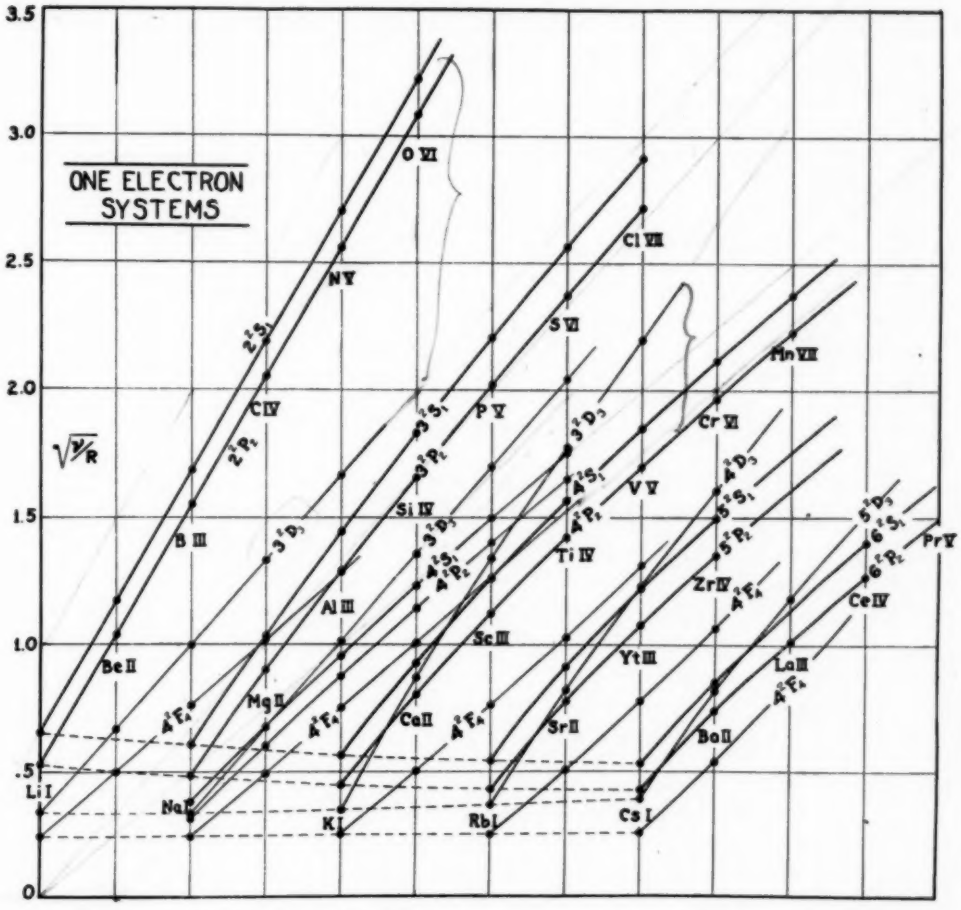

Fig. 2. Moseley diagram.

with the experiments on the magnetic susceptibility of cerium in solution, as explained by Hund,[10] in which he shows that the one remaining valence electron is an *f* electron.

In all three long periods the ^2D line crosses the ^2S line, Fig. 2, between the second and third elements showing that after the first two elements of each of these sequences the one valence electron in an unexcited atom is a *d* electron.

[10] Hund, Linienspektren und Periodisches System der Elemente, p. 179 (1927).

TABLE II. *Wave-lengths and frequencies of lines not previously reported.*

λ	ν	Diff.	Transitions
		Vanadium V	
481.657	207617	620	$3^3D_2-4^3P_2$
483.099	206997	1270	$3^3D_3-4^3P_2$
484.621	206347		$3^3D_2-4^3P_1$
1716.74	58250	1265	$4^3S_1-4^3P_1$
1680.26	59515		$4^3S_1-4^3P_2$
286.36	349211	634	$3^3D_2-4^3F_3$
286.88?	348577		$3^3D_3-4^3F_4$
820.89	121819	1267	$4^3P_1-5^3S_1$
829.52	120552		$4^3P_2-5^3S_1$
506.11	197585	1268	$4^3P_1-6^3S_1$
509.38	196317		$4^3P_2-6^3S_1$
		Chromium VI	
335.20	298311	957	$3^3D_2-4^3P_2$
336.30	297354	1822	$3^3D_3-4^3P_2$
337.28	296489		$3^3D_2-4^3P_1$
		Lanthanum III	
2216.83	45109.4	1602.8	$5^3D_2-6^3P_2$
2298.50	43506.6	3094.9	$5^3D_3-6^3P_2$
2380.13	42014.5		$5^3D_2-6^3P_1$

Wave-lengths and frequencies of lines not previously reported are given in Table II, for vanadium V, chromium VI, and lanthanum III.

CORNELL UNIVERSITY,
October 31, 1928.

QUANTUM ANALYSIS OF THE BERYLLIUM OXIDE BANDS

By Jenny E. Rosenthal and F. A. Jenkins

Abstract

New measurements of the structure lines in the (0, 0), (1, 1), (0, 1), (1, 2), (1, 0) and (2, 1) bands of the visible BeO system are reported. Each band has P and R branches of almost equal intensity, the lines of which are strictly single. There is probably but one missing line at the origin. This structure characterizes the system as $^1S \rightarrow {}^1S$, the odd multiplicity agreeing with the even number of electrons in neutral BeO. The rotational terms are investigated by the combination principle, and can be represented by $F(j)=Bj(j+1)+D[j(j+1)]^2+\cdots$ with j integral as required for ^1S states. One perturbation is found, consisting of a displacement of the line $R(49)$ in the (1, 0) band by 0.45 cm^{-1} toward lower frequencies, with no sign of doubling. The following equation is obtained for the null-lines: $\nu_0=21{,}254.05+1370.81(n'+\frac{1}{2})-7.76(n'+\frac{1}{2})^2-1487.45(n''+\frac{1}{2})+11.87(n''+\frac{1}{2})^2$.

Molecular constants of BeO.—The principal molecular constants, evaluated from rotational term-differences using the new quantum mechanics energy formula, are: $B_0'=1.5771$, $B_0''=1.6514$, $\alpha'=-0.0160$, $\alpha''=-0.0186$, $D_0'=-8.44\times10^{-6}$, $D_0''=-8.26\times10^{-6}$, $\beta'=+0.03\times10^{-6}$, $\beta''=-0.06\times10^{-6}$, $F_0'=22\times10^{-12}$, $F_0''=12\times10^{-12}$, the zero subscripts referring to the vibrationless condition. The nuclear separation in the final state is: $r_0''=1.327\times10^{-8}$ cm.

THE spectrum obtained by introducing beryllium or beryllium salts into the arc in air shows a system of bands in the visible region consisting of several sequences which degrade toward the red. The stronger band heads were first measured by Hartley, and later by Lecoq de Boisbaudran and by de Gramont.[1] The spectrum was investigated in more detail by L. C. Glaser,[2,3] using the second order of a 10-foot grating. In addition to more accurate and complete measurements of the heads, Glaser gave a table of the structure lines of the strongest sequence, that in the blue with its first head at λ4708. The lines of the first band he arranged in four series α, β, γ, δ. As will be shown below, this division cannot be justified, a fact which is not surprising since the work was done before the development of the present theory of band spectra. His attempts to find numerical relations between these bands and the AlO bands of the aluminum arc[4] were doubtless due to the marked similarity of the two spectra in many respects.

According to the view we wish to support, these beryllium bands are also due to the oxide, BeO. Some of Glaser's experiments give evidence for this; in particular he found that with the arc between metallic Be electrodes, the bands are much weaker in vacuum than in air. Further experimental evi-

[1] For a summary and comparison of the earlier results see Kayser and Konen, "Handbuch der Spectroscopie" VII, 102 (1924).

[2] L. C. Glaser, Dissertation, Berlin (1916).

[3] Glaser, Ann. d. Physik **68**, 73 (1922).

[4] W. C. Pomeroy, Phys. Rev. **29**, 59 (1927).

dence has recently been obtained by Jevons,[5] who finds this group of bands to be relatively stronger in the outer part of the flame surrounding the arc in air. Combining these observations with the theoretical confirmation to be given below, there seems to be little doubt as to the identity of the emitter. The purpose of the present communication[6] is to give the quantum interpretation of the rotational structure of the bands of this system. It is based on new measurements of the lines of the six strongest bands made from plates on which the dispersion and resolution are roughly double those reached by Glaser.

The spectrograms. A horizontal carbon arc with both poles cored with a mixture of equal parts of powdered potassium beryllium fluoride and carbon dust proved to be a very satisfactory source. With an average current of about 5 amp, a pale blue flame tinged with yellow appeared above the poles. An image of this flame was thrown on the slit of the 21 foot concave grating

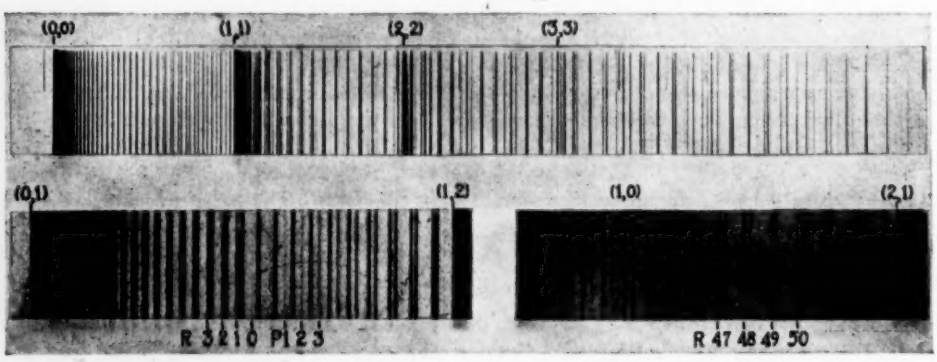

Fig. 1. *a*. Strongest sequence of BeO bands. Iron arc comparison spectrum. *b*. First part of (0, 1) band, showing intensity anomalies near the origin. The line $R(1)$ is exceptionally strong, while $R(0)$ is weaker than the corresponding line, $P(1)$. *c*. Region λλ 4435–4450 of the (1, 0) band. The perturbation of $R(49)$ shows as a discontinuity in the width of the doublets formed by R and P lines.

spectrograph.[7] The spectrum thus obtained consisted of the ultra-violet BeF bands,[8] the BeO bands in the blue and green, and the stronger bands of the green CaF sequence,[9] as well as atomic lines of Be, Ca, Fe, Mn and other impurities. Comparison lines of the iron arc were used[10] and their exact coincidence with the Fe lines appearing in the band exposure eliminated the possibility of accidental shifts.

[5] W. Jevons, Proc. Roy. Soc. (in press). We are indebted to Professor Jevons for making this article available to us in manuscript, as well as a copy of Glaser's work referred to above.[2]

[6] A preliminary account of this investigation was given in a paper before the American Physical Society at the New York meeting, February, 1928, Phys. Rev. **31**, 705 (1928).

[7] The plates were taken by one of the writers (F. A. J.) while a National Research Fellow at Harvard University. The characteristics of the grating and its mounting are described in Phys. Rev. **30**, 438 (1927).

[8] S. Datta, Proc. Roy. Soc. **A101**, 187 (1922).

[9] Datta, Proc. Roy. Soc. **A99**, 436 (1921).

[10] Wave-lengths as given by Meggers, Kiess and Burns, Bull. Bur. Stan. **19**, 263 (1924).

The strong group in the blue (Fig. 1*a*), according to the vibrational quantum number assignment made by Mecke,[11] is the sequence having $n''-n'=0$. The two adjacent sequences, $+1$ and -1, were also suitable for measurement. The $+2$ sequence found by Glaser and the few bands of the

TABLE I. *Lines in the visible BeO bands.* The columns of ν_{vac} for the lines of each band are headed by its vibrational quantum numbers and λ_{air} of the band head.

	(0,0) band λ4708.636		(0,1) band λ5054.415		(1,1) band λ4732.618		(2,1) band λ4451.664	
j	$R(j)$	$P(j)$	$R(j)$	$P(j)$	$R(j)$	$P(j)$	$R(j)$	$P(j)$
0	21,199.81							
1	202.88	21,193.25	19,739.14	19,729.70				
2	205.74	189.97	742.07	726.39	21,097.30			
3	208.52	186.41	744.89	722.96	099.76		22,439.22	
4	211.12	182.66	747.58	719.36	102.41	21,074.47	—	
5	213.58	178.88	750.21	715.73	104.82	070.69	444.00	22,410.20
6	215.58	174.82	752.63	711.95	107.12	066.71	446.14	—
7	217.71	170.65	754.96	708.02	109.19	062.61	447.93	401.84
8	219.65	166.35	757.19	704.04	111.20	058.37	449.68	397.49
9	221.43	161.93	759.40	699.92	112.99	054.02	451.23	392.84
10	223.12	157.28	761.48	695.70	114.68	049.50	—	388.11
11	224.62	152.57	763.43	691.4	116.32	044.91	—	383.11
12	225.92	147.70	765.30	686.89	—	040.13	454.75	378.03
13	227.23	142.69	767.03	682.33	118.65	—	455.47	372.76
14	228.40	137.53	768.64	677.82	120.05	030.17	456.18	367.29
15	229.34	132.22	770.12	673.05			456.70	361.70
16	230.08	126.75	771.51	668.22			457.23	355.95
17	230.67	121.01	772.79	663.26				350.00
18	230.94	115.39	773.95	658.20				343.89
19	—	109.40	774.98	653.06	(1,0) band λ4427.312		(1,2) band λ5075.726	
20	231.61	103.48	775.90	647.79	$R(j)$	$P(j)$	$R(j)$	$P(j)$
21	231.61	097.30	776.68	642.40				
22	—	090.96	777.37	636.95	0 22,555.06		19,651.13	
23	230.94	084.52	777.92	631.35	1 558.23		654.04	
24	230.67	077.93	778.40	625.65	2 560.82		657.07	19,641.47
25	230.08	071.17	778.84	619.92	3 563.51		659.76	638.05
26	229.34	064.31	779.18	614.00	4 565.93		662.56	634.56
27	228.40	057.30	779.18	608.04	5 568.11	22,534.03	665.09	630.93
28	227.53	050.17	779.18	601.94	6 570.16	529.79	—	627.28
29	226.33	042.88	779.18	595.66	7 571.98	525.41	669.89	623.43
30	224.94	035.41	778.84	589.35	8 573.67	520.90	672.26	619.48
31	223.48	027.85	778.40	582.92	9 575.17	516.23	674.46	615.49
32	221.75	020.03	777.92	576.38	10 576.49	511.34	676.57	—
33	219.95	012.30	777.37	569.76	11 577.65	506.27	678.55	607.29
34	218.01	004.20	776.68	563.04	12 578.57	501.08	680.49	602.81
35	215.97	996.02	775.90	556.20	13 579.29	495.63	682.32	598.54
36	213.58	987.65	774.98	549.24	14 579.87	490.09	683.93	594.06
37	211.12	979.40	773.95	542.27	15 580.30	484.34	685.52	589.36
38	208.52	970.73	772.79	535.08	16 —	478.39	686.98	584.61
39	205.74	962.02	771.51	527.90	17 580.79	472.16	688.32	579.73
40	202.88	953.18	770.12	520.51	18 —	466.09	689.60	575.01
41	199.81	944.17	768.64	513.02	19 580.30	459.64	690.70	569.84
42	196.56	935.02	767.03	505.50	20 579.87	452.83	691.71	564.85
43	193.25	925.77	765.30	497.86	21 579.12	446.14	692.64	559.73
44	189.67	916.36	763.43	490.05	22 578.28	439.22		
45	185.94	906.74	761.48	482.23	23 577.25	432.17		
46	182.11	897.07	759.40	474.37	24 576.06	424.86		
47	178.16	887.12	757.19	466.16	25 574.68	417.33		
48	173.97	877.08	754.80	458.01	26 573.10	409.68		
49	169.61	867.05	752.33	449.75	27 571.35	401.84		
50	165.15	856.75	749.71	441.39	28 569.43	393.84		
51	160.53	846.37	747.00	432.89	29 567.30	385.64		
52	155.72	835.82	744.19	424.31	30 564.94	377.32		
53	150.73	825.20	741.25	415.66	31 562.47	368.76		
54	145.57	814.25	738.17	406.89	32 559.76	360.13		
55	140.29	803.32	735.00	398.01	33 556.95	351.19		
56	134.87	792.21	731.67	389.03				
57	129.25	780.97	728.23	379.92				
58	123.58	769.48	724.65	370.72				
59	117.51	758.09	721.00	361.49				
60		746.40						
61		734.59						

-2 sequence recently added by Jevons[5] are very faint. Accordingly, measurements have been made of the lines of the first two bands in each of the three stronger sequences, using the second order except for the (0, 1) and (1, 2)

[11] R. Mecke, Phys. Zeits. **26**, 217 (1925).

bands, which were measured in the first order. The mean error for each line should not in general exceed 0.03 cm^{-1}. In some instances, however, because of superposition by atomic lines (particularly in the -1 sequence) and by other strong band lines, larger errors were unavoidable. Table I contains the wave-numbers in vacuum of all lines measured. In view of these numerous cases of superposition and overlapping of series, the intensity data are of very little value and have therefore been omitted.

Structural features of the bands. Since the bands of each sequence are closely grouped, the system is of the familiar type in which the vibration frequency and moment of inertia are only slightly changed by the electron transition. The vibrational intensity distribution is also characteristic of this type, resembling that of the violet CN bands in the arc. Hence there could be no doubt as to the correct assignment of vibrational quantum numbers. A complete description of the vibrational structure is given by Jevons[5] who finds that the heads are closely represented by:

$$\nu_A = 21{,}287.0 + 1364.2(n'+\tfrac{1}{2}) - 5.90(n'+\tfrac{1}{2})^2 - 1479.1(n''+\tfrac{1}{2}) + 15.22(n''+\tfrac{1}{2})^2 - 5.24(n'+\tfrac{1}{2})(n''+\tfrac{1}{2}) \quad (1)$$

The rotational structure is of the simplest possible type, each band having one R and one P branch of strictly single lines. Resolution is complete except for 4 or 5 lines at the head, and in the (0, 0) band about 70 members of each branch can be traced reaching a maximum of intensity between $j=30$ and 35 and extending over several other bands of the sequence. There is no sign of splitting into finer components even for the last lines. The α and β series of Glaser together make up the P branch, alternate lines belonging to one or the other. His γ and δ series form the R branch in a similar way.

Difficulty was encountered in establishing the number of missing lines, although the bands are well resolved in the neighborhood of the origin, which is far from the head. In the (0, 0) band, coincidence with the R lines returning from the head prevents any decision. The region of the origin in the (1, 0) band is obscured by a diffuse atomic line. The best evidence was obtained from the (0, 1) band. Here it appears that but one line is missing, although the first P line is extremely weak, and the first R line even stronger than two subsequent lines of this branch (Fig. 1*b*). The latter anomaly is very probably due to coincidence with the Ti line λ5064.66. No evidence was found of a Q branch, although a systematic search was made for Q lines of low intensity.

In the (1, 0) band a perturbation occurs which is obvious even on casual inspection (Fig. 1*c*). The line $R(49)$ is displaced 0.45 cm^{-1} toward lower frequencies from its expected position. The fact that no splitting or intensity change occurs is further evidence for the true singlet character of the lines. The corresponding line in the (0, 0) band is not perturbed, so the irregularity must be in the initial state $n'=1, j'=50$.

Rotational term analysis. Calling the first lines of the two branches $R(0)$ and $P(1)$ it was found at once that the combination relations between the R

and P branches[12] agreed among the bands in the manner to be expected. The extent of this agreement is shown graphically in Fig. 2. The combination differences Δ_2F for low quantum numbers are represented closely by $4B(j+\frac{1}{2})$ where $j=0, 1, 2 \cdots$. Since there is probably only one line missing near the origin and since the bands show no evidence of electronic multiplicity, the assumption is justified[13] that there is no resultant electronic angular momentum in either initial or final states. Hence the system arises from a transition

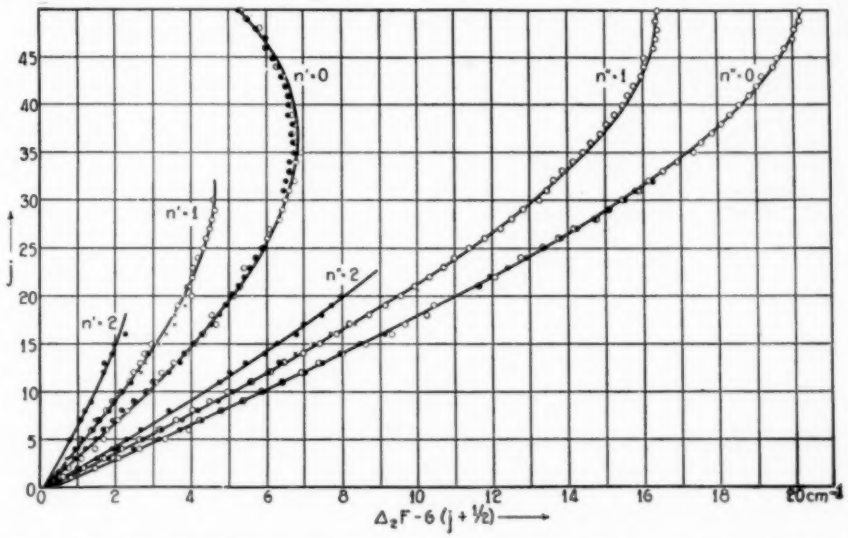

Fig. 2. Combination differences. The solid lines represent the values calculated by Eqs. (2) and (3). The linear function $6(j+\frac{1}{2})$ has been subtracted from Δ_2F to magnify the scale. For the initial states circles, dots and crosses represent data from bands having $n''=0$, 1 and 2, respectively. Similarly, for the final states they refer to bands with $n'=0$, 1 and 2.

between two $^1S_0$ molecular terms and is strictly analogous to the CuH bands. In a ^1S state the accurate expression for the rotational term-difference is, using the j values of the new quantum mechanics,

$$\Delta_2F(j)=4B_n(j+\tfrac{1}{2})+8D_n(j+\tfrac{1}{2})^3+12F_n(j+\tfrac{1}{2})^5+\cdots \qquad (2)$$

Following the method suggested by Birge[14] the constants B_n were evaluated by least squares, using the theoretical relations for D_n and F_n.[15] The results of this calculation are

$$\begin{aligned} B_n'&=1.5771-0.016(n'+\tfrac{1}{2}), & B_n''&=1.6514-0.0186(n''+\tfrac{1}{2}), \\ D_n'&=\{-8.44+0.03(n'+\tfrac{1}{2})\}10^{-6} & D_n''&=\{-8.26-0.06(n''+\tfrac{1}{2})\}10^{-6} \qquad (3) \\ F_n'&=22\times10^{-12} & F_n''&=12\times10^{-12}. \end{aligned}$$

[12] R. T. Birge, Bull. Nat. Res. Council No. 57, p. 145 (1926).
[13] R. S. Mulliken, Phys. Rev. **28**, 481 (1926).
[14] Ref 12, p. 174.
[15] Account was taken of the variation of D_n with n (ref. 4, Eq. (19)). F_n was taken as the same for $n=0$, 1 and 2.

From the constant terms in the equations for B_n, the following values of the moment of inertia I_0 for the vibrationless molecule and of the corresponding internuclear distances r_0 are obtained:

$$I_0' = 17.564 \times 10^{-40} \text{ gr cm}^2 \qquad I_0'' = 16.774 \times 10^{-40}$$

$$r_0' = 1.358 \times 10^{-8} \text{ cm} \qquad r_0'' = 1.327 \times 10^{-8}$$

B_n was evaluated separately for each band, and the agreements shown in Table II furnish conclusive evidence that the assignment of vibrational numbers is correct. This table also includes the band-origins, ν_0, each of which is

TABLE II. *Band constants*

	$n''=$ 0	1	2
n'	$B'=$ 1.5692	1.5689	
0	$B''=$ 1.6421	1.6232	
	$\nu_0=$21,196.76	19,732.99	
1	1.5534	1.5537	1.5537
	1.6422	1.6233	1.6052
	22,552.15	21,088.28	19,648.00
2		1.5363	
		1.6231	
		22,428.20	

the mean of a set of values obtained from several lines of both R and P branches. By the term formula used, ν_0 is the same as the wave-number of the null-line. The origins are quite accurately given by the equation:

$$\nu_0 = 21,254.05 + 1370.81(n'+\tfrac{1}{2}) - 7.76(n'+\tfrac{1}{2})^2 - 1487.45(n''+\tfrac{1}{2}) + 11.87(n''+\tfrac{1}{2})^2 \qquad (4)$$

Conclusions. The constants of the vibrational energy from Eq. (4) differ markedly from those given by Jevons (Eq. (1)). This is to be expected, since his equation refers to heads, which in the present case are at a rather large, and therefore variable, distance from the origins.

As was mentioned above, the rotational structure conforms in every respect with that to be expected for a band system resulting from a $^1S \rightarrow {}^1S$ electron transition. The odd multiplicity requires[13] that the emitting molecule have an even number of electrons. This definitely excludes BeN and BeH, leaving as possibilities Be_2 or BeO, since ionized molecules do not come into consideration. The experimental evidence favors BeO, as do considerations of stability. The internuclear distance in the final state, the lowest known level of BeO, as compared with the corresponding r_0 values for the oxides of the other elements in the first row of the periodic table seems entirely consistent with this view:

	BeO	BO	CO	NO	O_2
r_0''	1.33	1.21	1.15	1.15	1.20

All of these refer to the normal electronic state, and they evidently show the same general trend as the atomic volume curve for these elements.

NEW YORK UNIVERSITY,
UNIVERSITY HEIGHTS, N. Y.,
November, 1928.

THE IONIZATION BY SLOW ELECTRON IMPACT OF AMMONIA AND HYDROGEN SULPHIDE

By James H. Bartlett Jr.

Abstract

The molecules of ammonia and hydrogen sulphide have been studied by the usual method of positive-ray analysis, such as used by Dempster, Smyth, and others. In the case of ammonia, three principal types of ion at $m/e=15$, 16 and 17, respectively, occurred. These are interpreted as having the compositions $(NH)^+$, $(NH_2)^+$, and $(NH_3)^+$, with *ionization potentials* of 11.2 ± 1.5 volts, 12.0 ± 1.5 volts, and 11.2 ± 1.5 volts, respectively. Since, with increasing pressure, the $(NH)^+$ ion increases, the $(NH_2)^+$ ion remains sensibly constant, and the $(NH_3)^+$ ion decreases, it is concluded that the $(NH_3)^+$ and $(NH_2)^+$ ions result directly from the electron impact with the neutral NH_3 molecule, while the $(NH)^+$ ion is probably produced by breakdown of the $(NH_3)^+$ ion by a reaction such as $(NH_3)^+ + NH_3 = (NH)^+ + H_2 + NH_3$. For both ammonia and hydrogen sulphide, very few, if any, hydrogen ions and no negative ions were observed, tending to show that thermal dissociation was of little importance in affecting the results. For ammonia, very small peaks at $m/e=14$ and 18, respectively, were observed. Their compositions are probably $(N)^+$ and either $(NH_4)^+$ or $(H_2O)^+$, and their origin is either secondary (from collision of ions with neutral molecules) or they result from impurities. In the case of hydrogen sulphide, three principal types of ion were likewise observed. They occur at $m/e=32$, 33, and 34 and are interpreted as having the compositions $(S)^+$, $(HS)^+$, and $(H_2S)^+$, respectively. Using Mackay's value of the lowest ionization potential as a standard for the calibration of the voltage scale, the *ionization potentials* are approximately 10.4 volts, 16.9 volts, and 15.8 volts, respectively. Variation of the pressure, at low pressures, indicates that no secondary processes occur, i.e. that the ions above named are all formed by the initial process of the electrons colliding with the gas molecules. No S_2^+ ions were observed, nor any which could be due to isotopes of sulphur.

IN AN attempt to evolve systematic rules concerning the structure of molecules, progress is hastened if a wealth of empirical data concerning their behavior is at hand. While many diatomic molecules have been investigated[1] by the method of positive-ray analysis, comparatively little has been done in the field of more complex molecules. Accordingly, after an investigation of the water vapor molecule[1] in conjunction with Dr. Barton, the above method was likewise applied to the study of the ammonia and hydrogen sulphide molecules.

Ammonia[2]

Ammonia was evaporated from a chemically pure ammonium hydroxide solution, and dried thoroughly over potassium hydroxide sticks. That these were efficient was evidenced by the very small proportion of water vapor ions which was observed, if any.

[1] For details and references to the literature, see H. A. Barton and J. H. Bartlett Jr., Phys. Rev. **31**, 822 (1928). A comprehensive view of the work done and an attempt at interpretation is given in an article by R. S. Mulliken, Phys. Rev. **32**, 186 (1928). See also T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 784 (1928).

[2] A preliminary report has been published, Phys. Rev. **31**, 1129 (1928).

At low pressures, of the order of less than 10^{-4} mm, a mass spectrum such as is shown in Fig. 1 was obtained. If water vapor be admitted to the apparatus with no ammonia present, then the usual peaks at m/e of 17 and 18 are found. This, together with an additional calibration of the mass scale by the admission of nitrogen, indicates that the peaks here shown correspond to ions of $m/e=15$, 16, 17, and 18. The occurrence of the peak at $m/e=17$ cannot be due to the formation of the ion $(OH)^+$, since this occurs in lesser amounts[1] than $(H_2O)^+$, and it is seen from the figure that the peak at $m/e=18$ is quite small in comparison with that at $m/e=17$. In addition, the presence of the peak at $m/e=16$ is not to be interpreted as due to $(O)^+$, since especial care was taken in introducing the ammonia so that no such impurity could be present in appreciable quantities. Further evidence is furnished by the value of the ionizing potential found for each type. It seems, therefore, justifiable to assign to the ion at $m/e=17$ the composition $(NH_3)^+$ and to that at $m/e=16$ the composition $(NH_2)^+$. A distinct peak appears at $m/e=15$, and the only logical interpretation evident is that which assigns to it the composition $(NH)^+$.

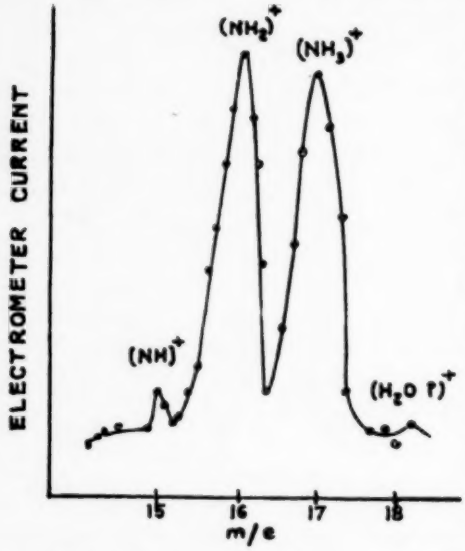

Fig. 1. Mass spectrum of ions produced by electron impact in ammonia, low pressure.

The character of the mass spectrum at higher pressures, of the order of 20×10^{-4} mm, is indicated by Fig. 2. The $(NH)^+$ peak has become more intense and the $(NH_3)^+$ peak less so. There is distinct evidence of peaks at $m/e=14$ and 18. The composition of the former peak is doubtless $(N)^+$, while that of the latter peak may be due to $(NH_4)^+$, or possibly $(H_2O)^+$. The latter alternative is possible, since there was no convenient method of ascertaining whether or not the gas was absolutely dry.

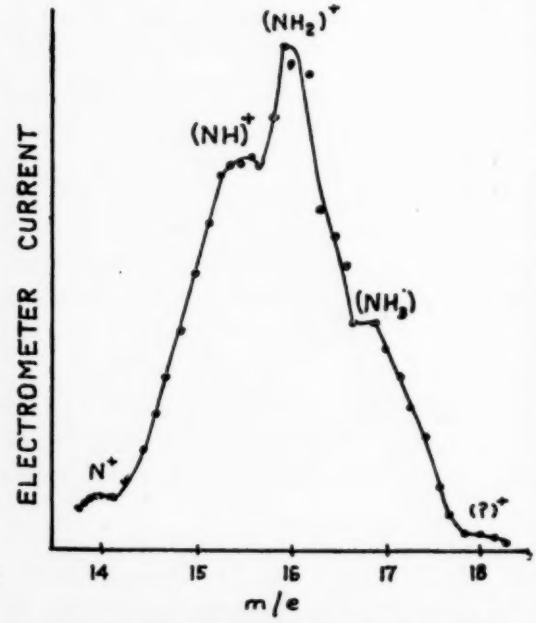

Fig. 2. Mass spectrum of ions produced by electron impact in ammonia at higher pressure.

No negative ions, and few, if any, hydrogen ions were observed. This latter fact tends to indicate that thermal dissociation processes do not play an important rôle. This is probably due to the rapid motion of the gas through the tube together with the fact that collisions take place at some distance from the filament, an arrangement recommended by Waldie,[3] who found that ammonia is almost entirely dissociated in the immediate neighborhood of the filament.

A comparison of the ionizing potentials for $(NH_3)^+$, $(NH_2)^+$, and $(NH)^+$ is shown in Fig. 3. The three curves were plotted from three consecutive runs made under quite favorable conditions, although the curve for $(NH)^+$ probably shows in its curvature the effect of a somewhat unsteady filament

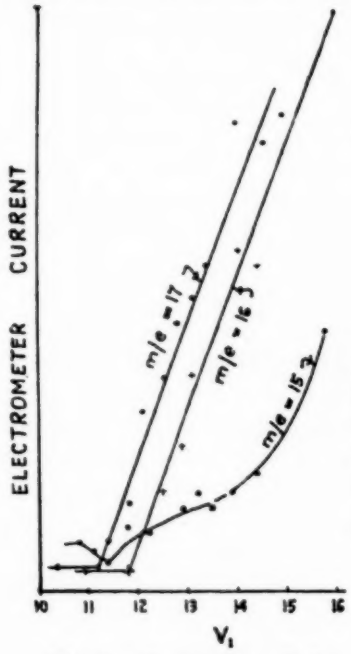

Fig. 3. Comparison of the ionizing potentials for $(NH_3)^+$, $(NH_2)^+$ and $(NH)^+$.

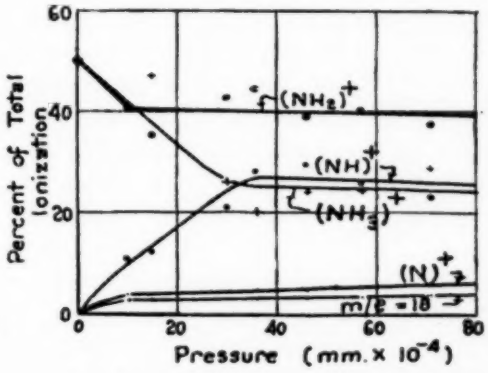

Fig. 4. Relative proportions of different types of ions as a function of pressure.

emission current. Its ionization potential, however, is fairly definite, and is about 11.2 ± 1.5 volts. There is an apparent difference between the ionization potentials for $(NH_3)^+$ and for $(NH_2)^+$, that for the former being 11.2 ± 1.5 volts, a mean of twelve observations, and that for the latter being 12.0 ± 1.5 volts, a mean of ten observations. These observations were weighted in accordance with the sensitivity of the apparatus, as determined by the peak height at a definite V_1, in this case 18 volts. The ionization potential of $(NH_3)^+$ is in good agreement with that of 11.1 volts observed by Mackay,[4] and with that of 11 volts observed by Waldie.[3]

[3] A. T. Waldie, Frank. Inst. J. **200**, 507 (1925).
[4] C. A. Mackay, Phys. Rev. **24**, 319 (1924).

Fig. 4 shows how the relative proportions of the different types of ion vary with the pressure. The $(NH_3)^+$ and $(NH_2)^+$ ions are present even at the lowest pressures and are probably the direct result of the electron impacts on the ammonia molecules, which is attested to by the observations that the ionization potentials for the two types were different. Since the relative amount of the $(NH)^+$ ion increases with increasing pressure from a small amount at low pressures, it must be largely, if not wholly, a secondary ion. Further, since its increase is similar to the decrease of the $(NH_3)^+$ type, it seems probable that there occurs a reaction of some such type as: $(NH_3)^+ + NH_3 = (NH)^+ + H_2 + NH_3$. The $(NH_2)^+$ ion seems to be more stable than the $(NH_3)^+$ ion, since its relative amount does not vary greatly within the range of pressures used. The $(N)^+$ type increases slightly with increasing pressure, and is probably a secondary type, although possibly an impurity. The ion at $m/e = 18$ also increases slightly with pressure. Nothing absolutely definite can be said as to its nature, in view of the alternatives $(NH_4)^+$ and $(H_2O)^+$, and since it occurred in such small quantities that its ionization potential could not be measured with certainty.

The main points of the above interpretation are not out of harmony with results obtained by other investigators, in that excited (and therefore probably ionized) molecules with compositions NH_3, NH_2, and NH are supposed to exist. In the visible spectrum of ammonia there are dominant the Schuster bands, supposedly due to NH_3, and the α-bands, which probably originate[5] from both NH_3 and NH_2. In the ultra-violet region there occur the β-bands, which resemble the known hydride bands in some respects and so are thought [6,7,8] to be emitted by the NH molecule. Thus, it is to be expected from spectral observations that one would find exactly those principal types of ion which have been observed in this research.

Hydrogen Sulphide

Hydrogen sulphide, presumably 99.7 percent pure, was obtained from the Mathesen Co. in an ordinary lecture bottle. Special precautions were taken so that no air could be mixed with the gas as it was introduced to the system. After the usual process of solidification and evaporation to eliminate water vapor and other possible impurities, the gas was stored over phosphorus pentoxide before its final admission to the system. In order to protect the metal parts of the apparatus from the chemical action of the gas, an additional pump was connected to the storage chamber, so that large quantities of excess gas could be pumped off without passing through the main system. The gas was purified from time to time by solidification and evaporation in a liquid air trap. In the study of both hydrogen sulphide and ammonia, tungsten filaments were used for the most part, and proved quite satisfactory.

A typical mass spectrum is shown in Fig. 5. The resolving power of the apparatus was sufficient to distinguish between three types of ion, spaced one unit apart on the m/e scale, which was calibrated with the aid of water vapor and air. The peaks here shown are thereby identified as having

[5] W. B. Rimmer, Proc. Roy. Soc. **A103**, 696 (1928).
[6] E. Hulthén and S. Nakamura, Nature **119**, 235 (1927).
[7] S. Barrat, Proc. Roy. Soc. **A98**, 40 (1920).
[8] E. Gaviola, Nature **122**, 313 (1928).

m/e's of 32, 33, and 34, respectively. Without doubt, the two latter peaks correspond to ions of composition $(HS)^+$, and $(H_2S)^+$, respectively. In the case of the former peak, however, it is imperative to make certain that one is not dealing with $(O_2)^+$ in addition to $(S)^+$. The presence of air mixed with the hydrogen sulphide may be detected by the quite low intensity of ionization observed, by the presence of a large peak at $m/e=28$ corresponding to $(N_2)^+$, by the rapid burning out of filaments (in the case of tungsten filaments), and by the existence of an ionizing potential for the $m/e=32$ peak of approximately 13 volts. The second test is the most certain criterion, although at high filament temperatures there is a small peak at $m/e=28$ due probably to $(CO)^+$ from the waxes in the tube. It was found possible to eliminate any impurity such as air, so that all these four tests showed its absence. The peak with $m/e=32$ still persisted and must be interpreted as having the composition $(S)^+$ alone. These three peaks are mentioned by Aston.[9] As he found, so it was found here that there is no evidence of peaks at $m/e=35$ or 36, which, if existent, would indicate isotopes of sulphur at $m/e=33$ or 34, respectively. No $(S_2)^+$ ions were observed.

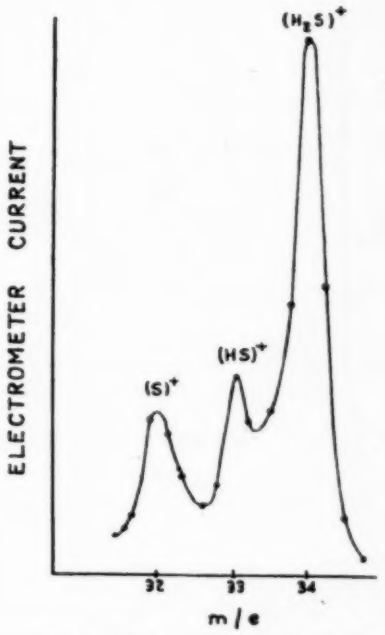

Fig. 5. Mass spectrum of ions produced by electron impact in H_2S.

A definite ionization potential was found for each of the three types of ion. That for $(H_2S)^+$, the weighted mean of fourteen observations is 11.1 ± 1.5 volts, in approximate agreement with the value given by Mackay,[4] who concluded that there was a discontinuity at 10.4 volts due to $(H_2S)^+$, the identification of the ion involved being confirmed here. The discrepancy may be due either to uncertainty in the electron speeds or to chemical reaction with the grid, which might affect the field somewhat. The results here obtained indicate that dissociation processes due to the electron impacts occur. There is positive evidence of an $(HS)^+$ peak with an ionization potential of 17.6 ± 1.5 volts (the weighted mean of ten observations). The range of Mackay's measurements just falls short of this and may explain our disagreement with his conclusion as to the non-existence of dissociation products due to electron impacts. The thermal dissociation does not become of any importance, however, in affecting our results, since hardly any hydrogen ions (and no negative ions) were observed, and the ionization potential of $(S)^+$, namely 16.5 ± 1.5 volts (the weighted mean of twelve observations), indicates that it arises from H_2S by electron impact, rather than from a sulphur atom. Since Mackay's work on H_2S was done with an apparatus designed primarily

[9] Aston, Isotopes (1924) p. 79.

for the measurement of ionization potentials, it seems best to adopt his value of 10.4 volts as a calibration of the absolute voltage scale, so that the corrected values of ionization potentials are (1) for $(H_2S)^+$, 10.4 volts, (2) for $(HS)^+$, about 16.9 volts, and (3) for $(S)^+$, about 15.8 volts.

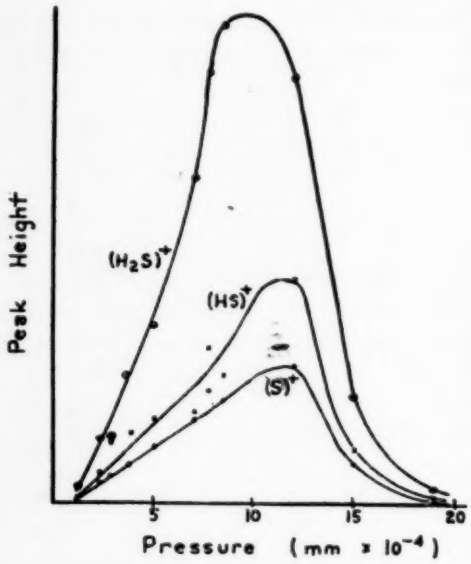

Fig. 6. Relative proportions of different types of ions as a function of pressure.

The characteristic curves of pressure variation are shown in Fig. 6. It is seen that there is no evidence of any secondary process taking place and that the relative proportions of the different types of ion remain sensibly constant as the pressure is increased. From this and from the existence of distinct ionization potentials, it is to be concluded that the three types of ion are all due to the primary process of electron impact with molecules of hydrogen sulphide.

Discussion

As in previous cases, so it is found here that the principal molecular ions, namely $(NH_3)^+$ and $(H_2S)^+$, are formed by the primary process of electron impact. In addition, other such "primary"[1] ions are found, namely $(NH_2)^+$, $(HS)^+$, and $(S)^+$. It seems to the writer that very little can be said with any degree of certainty about the way in which the latter ions are formed, in view of the very incomplete knowledge[10,11] of the molecular structure as found to date from the band spectrum data. The conjecture[5] that the $(NH_2)^+$ and $(NH)^+$ ions are more stable toward collisions than the $(NH_3)^+$ ion finds support in the results given here. The fact that the ammonia and hydrogen sulphide molecules are easily dissociated thermally indicates a weak binding and would lead one to believe that these molecules might also be dissociated by electron impact. This view likewise finds support in the present results.

In conclusion, the writer wishes to express his appreciation to Dr. H. A. Barton and Professors E. C. Kemble and P. W. Bridgman for many helpful suggestions, and to Mr. H. W. Leighton for material assistance in glass-blowing. (This work was carried out at the Jefferson Physical Laboratory of Harvard University.)

Institut für Theoretische Physik,
Leipzig,
October 15, 1928.

[10] From the symmetry characters of a possible model, the type of NH_3 spectrum to be expected has been predicted by F. Hund, Zeits. f. Physik **43**, 823 (1927).

[11] See also for NH_3, R. M. Badger, Nature **121**, 942 (1928), and B. J. Spence, Jour. Opt. Soc. Amer. **10**, 127 (1925). See also Robertson and Fox, Proc. Roy. Soc. **A120**, 189 (1928).

THE EFFICIENCY OF ELECTRON IMPACT LEADING TO RESONANCE IN HELIUM

By George Glockler

Abstract

The efficiency of resonance impact between electrons and helium atoms has been studied as a function of the energies of the impinging electrons. The transition studied is $1^1S \rightarrow 2^3S$ at 19.77 volts. The range of energies is 0.8 volt, i.e. from 19.77 to 20.55 volts. The efficiency with which electrons make inelastic impacts rises to a maximum 0.18 volts beyond the resonance potential of 19.77 volts and then decreases. The maximum average efficiency for electrons of 19.95 volts energy is estimated to be 0.002. The measurements were carried out by comparing the velocity distribution of the electrons leaving an equipotential surface with the drop in current as observed in the inelastic impact method of Franck, and similarly by comparing the velocity distribution of the electrons with the distribution of the positive current caused by them in a Lenard experiment. Both types of measurement yield similar results.

1. *INTRODUCTION.* In order to further our understanding of the mechanics of collisions between electrons and atoms it is important to determine the probabilities of such collisions. For the case of ionization several investigations have been made.[1] It appears that the efficiency of ionization, which is zero below the ionization potential, gradually *increases* from zero to 0.1 to 0.3 at optimum speeds of from 70–160 volts for various gases. The case of resonance efficiency has been studied by Sponer[2] who measured the average efficiency for electron impacts in mercury vapor and by Dymond[3] who studied the first critical potential of helium. Sponer's work would indicate that the efficiency of excitation is large right near the resonance potential and then decreases with increasing energy of the impinging electron. K. T. Compton[1] deduced a similar relation of efficiency and electron energy from the measurements of the photoelectric current in mercury vapor by Franck and Einsporn.[4] Sponer finds an average efficiency of about 0.004 for excitation of mercury atoms by electrons having energies between 5 and 6 volts. Hertz[5] has recalculated her results using a different value for the total number of impacts that an electron makes in crossing the space between filament and plate in Sponer's experiments, and finds for the average efficiency 0.03. Dymond, however, finds that the efficiency of excitation in helium rises to a maximum 0.25 volt above the first resonance potential (19.77 volts), and then decreases to one fourth the maximum value at 0.5 volt above the critical potential. He calculates the maximum efficiency to be 0.001.

[1] Compton and Mohler, Bull. Nat. Research Council, No. 48, 52 (1924); also Compton and Van Voorhis, Phys. Rev. **26**, 436 (1925).

[2] H. Sponer, Zeits. f. Physik **7**, 185 (1921).

[3] G. Dymond, Proc. Roy. Soc. **A107**, 291 (1925).

[4] Franck and Einsporn, Zeits. f. Physik **2**, 18 (1920).

[5] G. Hertz, Zeits. f. Physik **32**, 298 (1925).

From these investigations it is seen that the efficiency of ionization and of resonance are dependent on electron energies in quite a different manner and that their numerical values are of a different order of magnitude. In this paper the probability of excitation of helium has been studied. The transition $1^1S \rightarrow 2^3S$ leading from normal par-helium to metastable ortho-helium has been investigated from 19.77 to 20.55 volts.

2. *Experimental procedure.* The experimental arrangement used has been fully described in a previous paper.[6] In our further discussion we shall call the space between the emitting surface and the first gauze, which is at a distance of one millimeter from the emitter, the first condenser. In this region electrons receive energy from the accelerating field A_1. They will not make many impacts with gas molecules before they enter the space between the two gauzes which is the second condenser. The distance between the two gauzes is 1.1 cm and here the electrons make impacts with the gas molecules. The third condenser is the region between the second gauze and the receiving plate and is of small dimension (one millimeter between second gauze and plate). A small retarding field is applied in the Franck experiment to keep electrons that have lost their energy because of inelastic impact in the second condenser from reaching the plate and a large retarding field is applied in a Lenard experiment to keep all primary electrons from the plate, but to attract positive ions to or remove photo-electrons from the plate.

3. *Types of current-potential curves.* With the experimental arrangement described above it is possible to obtain four types of current-potential curves. The actual experimental curves are shown in Fig. 2 of the previous paper.[6] In the present paper we wish to compare the shapes of these curves with one another and in order to carry out this comparison we have replotted the experimental curves by taking the differences of the ordinates (galvanometer deflections) for each one-tenth volt interval. We then gave to the maximum ordinate of these difference curves of each type the same numerical value by multiplying the ordinates with an appropriate factor and then we averaged them by taking the mean value of the ordinates at the same abscissaand in this way we obtained one *average* current-potential curve representing each of the four types of experimental curves given in the previous paper. The maximum ordinates of our four types of difference curves have all been made 2.68 on an arbitrary scale. The other points vary each about a mean value. The average deviation from the mean ordinate is given in the tables. While the average deviation is large especially near the ends of the distribution curves, it should be noted that this is partly brought about by our method of averaging the curves. We have arbitrarily taken the middle point (the maximum ordinate) the same for all the curves and naturally the error would thereby tend to accumulate near the ends of the curves. By doing so we have given more weight to the greater changes in galvanometer deflection and this procedure seems reasonable because the differences in deflection near the ends of these curves are smaller and therefore less accurate. It will be seen in the course of our discussion that the accuracy of these points is

[6] G. Glockler, Phys. Rev. **27**, 423 (1926).

sufficient, for our argument rests only on the most general shape of these curves and upon the volt values of their maximum ordinates. The individual curves are now to be described in detail.

4. *The electron velocity distribution* (*Method I*). The distribution of the initial velocity of the electrons emitted by the filament has been obtained by two methods. The current-potential curves giving this distribution were obtained in the first method by the use of a constant accelerating field A_1 in the first condenser and a varying retarding field R_2 in the second condenser. The six experimental curves of Fig. 2-*A* of the previous paper give an average curve and the quantities used to plot this curve are given in Table I, columns 2 and 3. The ordinates G_n are proportional to the decrements of the galvanometer deflections, and the abscissae give the range of the initial velocity and contact potential corrections.

TABLE I. *Electron velocity distribution*

A_1 is the accelerating field. R_2 the retarding field. G_n is the increase or decrease in the galvanometer reading for each 0.1 volt interval.

Interval n	Method I		Method II		Average
	(R_2-A_1)	G_n	A_1	G_n	G_n
1	0.66±0.05	0.08±0.01	0.31±0.05	—	0.08
2	0.76	0.15±0.06	0.41	—	0.15
3	0.86	0.33±0.07	0.51	0.27±0.06	0.30
4	0.96	0.70±0.10	0.61	0.79±0.10	0.75
5	1.06	1.50±0.11	0.71	1.53±0.10	1.52
6	1.16	2.36±0.06	0.81	2.27±0.07	2.31
7	1.26	2.68±0.00	0.91	2.68±0.00	2.68
8	1.36	2.19±0.05	1.01	2.20±0.10	2.20
9	1.46	1.11±0.08	1.11	1.32±0.17	1.21
10	1.56	0.16±0.04	1.21	0.76±0.14	0.76
11	1.66	—	1.31	0.48±0.10	0.48
12	1.76	—	1.41	0.25±0.08	0.25
13	1.86	—	1.51	0.12±0.04	0.12

5. *The electron velocity distribution* (*Method II*). We have also obtained the velocity distribution of the electrons by measuring the electron stream leaving the filament (with helium in the apparatus) as a function of the accelerating field A_1 applied to the first condenser. The increase in electron current to the first grid was measured as the first accelerating field was increased from 0.5 volt to 1.5 volts while the other fields were zero. The curves of Fig. 2-*F* and 2-*G* of the previous paper show this electron current. We have now averaged these eight curves and we have arbitrarily chosen the ordinates of galvanometer deflections G_n in such a way that the maximum ordinate of the difference curve is 2.68. The abscissae give the range of the initial electron velocity and contact potential corrections. The data are given in Table I (columns 4 and 5).

In our reduction of the experimental curves we have corrected for the constant increase in electron-current to the plate as the first accelerating field is increased. It is well known that saturation is not reached in the usual set-up. The correction has been made by subtracting the constant increment

that appeared in the electron-velocity distribution curve taken in helium. A similar correction was made in the Franck curve. We have studied our data both with and without making this correction and we find that its use does not effect the results of our analysis. The correction has only a slight effect on the shape of the curves.

6. *Comparison of the electron velocity distribution curves.* The data of Table I are averaged in the last column by making the maxima of the curves coincide and the average electron velocity distribution curve is shown in Fig. 1. It is seen that the velocity distribution obtained by the two methods is the same. When it is considered that the conditions under which these two types of curves were obtained are quite different, that however the distribution curves obtained are quite similar, it is evident that any disturbing factors such as random direction of electrons and secondary electron emission are not of sufficient magnitude to vitiate the results. It should be noted that the retarding potential in the first method is applied in the second condenser and it will affect the whole energy of the electron, because of the more or less spherical construction of the electrodes, and not only one component. In Table I column 3 it is noted that the change in current after the ninth interval is less than in Method II (column 5). This lack of agreement may be due to secondary emission. It is evident that the two methods check very well near the maximum point and this section of the distribution curve is the one of greatest interest to us.

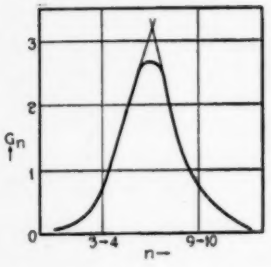

Fig. 1. Average electron velocity distribution curve.

The voltage range in Table I is one-tenth volt. For example, the point 1.26 volts (second column) means that the current to the plate dropped 2.68 units while the voltage changed from 1.21 to 1.31 volts. Similarily the voltage values given in all of the tables always refer to a range of one-tenth volt, the

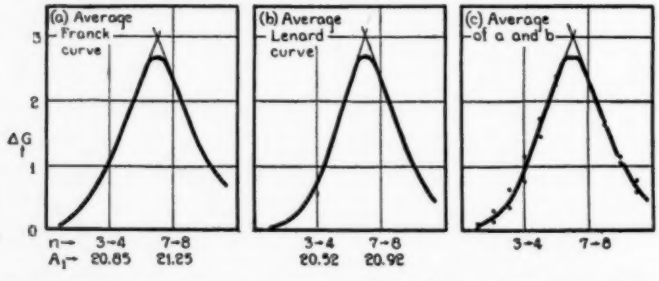

Fig. 2. *a.* Distribution curve of drop in current in Franck experiments. *b.* Distribution curve of rise in current in Lenard expeirments. *c.* Comparison of *a* and *b.*

mean value of the range being given in the table. The volt values in Table I given for the two methods differ by 0.35 volts. This difference is due to a change in contact potential as noted in the previous paper. The distribution curves shown in Figs. 1 and 2 are drawn in such a manner that the fast electrons or the current caused by them is always shown on the left side of

the figure. The intervals "n" given in the first column of the tables are a convenient notation and they give the changes in current for one-tenth volt change in voltage. The numbering of these intervals is accomplished by giving the first interval the number "one" when the galvanometer current (G_n or ΔG_n) rises from zero to the first noticeable reading.

7. *The current drop* (*Franck Method*). The drop in current near twenty volts obtained by the inelastic impact method of Franck is shown in Fig. 2-*B* and *C* of the previous paper. The current-potential difference curves have been reduced to an arbitrary maximum ordinate of 2.68 and in Fig. 2*a* the average curve of nine experiments is shown. The ordinates are the decrements in the drop in electron current reaching the plate and the abscissae are the increments in the applied accelerating field in the first condenser expressed in volts uncorrected for contact potential. The data for Fig. 2*a* are given in Table II. The correction for the constant increase in current with increase in A_1 has been made.

8. *The current rise* (*Lenard Method*). In this method the electron current to the plate is zero on account of the large retarding field of thirty volts applied in the third condenser. However, when either secondary or photoelectrons leave the plate or positive ions reach it, a positive current results. This happens near twenty volts. This rise in positive current to the plate is shown in Fig. 2-*H* and 2-*I* of the previous paper. Again the eight difference curves shown there have been united into an average curve with arbitrary ordinates. The maximum ordinate has been given the value 2.68 on an arbitrary scale. The average curve is shown in Fig. 2*b* and the necessary data in Table 2.

9. *Comparison of Franck and Lenard curves.* The Franck curves (Fig. 2*a*) are compared with the Lenard curves (Fig. 2*b*) as is shown in Fig. 2*c*. *The two types of current-potential curves are similar in shape.* The Franck curve gives a picture of the "zero-volt" electrons produced when the electron stream from the filament makes inelastic impacts with helium atoms and the Lenard-curve gives a measure of photoelectrons (or positive ions of an impurity) produced under the same conditions. Both are the effect of the interaction of the primary electron stream with helium atoms, when the primary stream has reached sufficient energy to cause the resonance transition $1^1S \rightarrow 2^3S$. It may then be expected that the two curves should be identical in shape.

We shall assume that the difference which exists between the shapes of the Franck and Lenard curves is due to experimental error. We have therefore averaged the two curves and the averaged data are given in the last column of Table II. The averaged Franck-Lenard curve is shown in Fig. 2*c*.

The question arises what effect secondary electrons would have on the shapes of these curves. If, for instance, the Franck curve includes secondaries then the real ΔG_n values would be larger. If, however, the fraction of secondaries emitted is constant in the small voltage range considered (which is not unreasonable) then the shape of the difference curves described above is not affected, since we always plot them to an arbitrary scale. In the electron velocity curves we deal with very slow electrons which are known not to emit secondaries and in the Lenard curves we have no primaries reaching the

plate. Secondary emission should then have no marked effect on the shapes of our curves although numerical values would be affected.

TABLE II. *Comparison of current drop in the Franck experiment and current rise in the Lenard experiment*

Interval n	Franck experiment $A_1 \pm 0.05$	Franck experiment ΔG_n	Lenard experiment $A_1 \pm 0.05$	Lenard experiment ΔG_n	Average ΔG_n
1	20.55	.10 ± .04	20.22	.04 ± .06	.07
2	.65	.32 ± .12	.32	.13 ± .09	.23
3	.75	.66 ± .13	.42	.35 ± .12	.50
4	.85	1.15 ± .09	.52	.77 ± .16	.96
5	.95	1.73 ± .09	.62	1.46 ± .15	1.60
6	21.05	2.38 ± .08	.72	2.26 ± .12	2.32
7	.15	2.68 ± .00	.82	2.68 ± .00	2.68
8	.25	2.34 ± .11	.92	2.34 ± .12	2.34
9	.35	1.68 ± .24	21.02	1.66 ± .14	1.67
10	.45	1.13 ± .30	.12	1.05 ± .15	1.09
11	.55	0.77 ± .28	.22	.58 ± .11	.68

10. *Comparison of electron velocity distribution curve and Franck and Lenard-curves.* The average electron velocity distribution (last column Table I) and the average Franck-Lenard curve (last column Table II) are shown in Fig. 3. The maxima of these curves have been made to coincide. From the values of the abscissae of these maximum ordinates we find the experimental values of the first resonance potential of helium:

TABLE III. *Comparison of values of first critical potential in He as given by Franck and Lenard experiments with the spectroscopic value.*

	Franck expt.	Lenard expt.
Accelerating potential (uncorrected)	21.15 ± 0.06 volts	20.82 ± 0.02 volts
Correction	1.26 ± 0.01	0.91 ± 0.06
First resonance potential of He by electron impact	19.89 ± 0.07	19.91 ± 0.08
Spectroscopic value	19.77	19.77
Difference	0.12 ± 0.07	0.14 ± 0.08

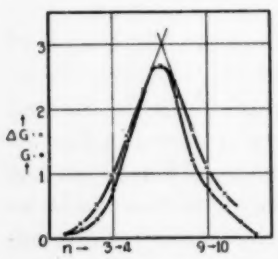

Fig. 3. Comparison of electron velocity distribution and current drop and rise in the Franck and Lenard experiments.

The two types of experiments yield the same result: namely, that *the shapes of the distribution curves are similar and that the maxima of these curves are displaced 0.13 volts.* The reason that the uncorrected values of the critical potentials and the corrections are different in the Franck and Lenard experiments has already been mentioned. The emitter had to be reconditioned after the Franck curves and before the Lenard curves had been taken, and the contact potential had been changed. The corrected values check satisfactorily. The correction of 0.91 volt applied to the Lenard curves had been given in the previous paper (page 428) as 1.00 volt. We have

taken in the present analysis in Method 2 of determining the initial velocity correction, the electron current to the first grid for it is much larger than the plate current and should give more accurate curves. The difference of 0.13 volt between the resonance potential as determined by electron impact and spectroscopy is not very accurate because it is determined as the difference of two large numbers. However, since both types of measurements yield the same average result we may accept it with some confidence.

In our further analysis we shall need to know the total number of impacts that an electron makes while crossing the gas-space in the condenser. This claculation can be made from kinetic theory on the assumption that the electron loses no energy on impact with a helium atom. However, it is known that an electron does lose energy even while making an elastic impact and we shall also calculate the number of impacts an electron makes on the assumption that the impact takes place in accordance with the laws of classical mechanics, while the electron changes its energy from 19.87 to 19.77 volts.

11. *The total number of impacts from kinetic theory.* It can be shown[7] that an electron in crossing the second condenser will make n impacts, where

$$n=(3/2)(a/l)^2 \tag{1}$$

and a is the thickness of the condenser and l is the mean free path of the electron at the gas-pressure p. The mean free path l_1 of helium[8] atoms at pressure p is from kinetic theory:

$$l_1=29.6\times 0.00075/p \text{ cm/mm Hg} \tag{2}$$

As is well known, the mean free path of a particle of small size, like an electron is $4\cdot 2^{1/2}$ times the mean free path of the atom. Furthermore, if we take into account the fact that the mean free path of an electron varies with its speed, as is known from the work of Ramsauer,[9] we must multiply the expression by 0.8, in order to obtain the mean free path for electrons of the velocity used. The thickness of the second condenser was 1.1 cm, but when we take into account the fact that the emitter and first gauze are semi-spherical in shape, while the second gauze and plate are cylindrical, we find from geometry that the average thickness of the second condenser is 1.3 cm. We have then for the total number of impacts in our apparatus.

$$n=164p^2 \tag{3}$$

12. *The total number of impacts from mechanics.* The above calculation has been made on the assumption that the impinging electron loses no energy when colliding elastically with a helium atom. However, Hertz[10] has shown that an electron does lose energy even during an elastic impact, and that this loss is the loss that occurs when solid hard spheres of the masses of the electron and helium atom collide. This loss can therefore be calculated from the

[7] G. Glockler, Proc. Nat. Acad. Sci. **12**, 178 (1926).
[8] S. Dushman, High Vacuum, Gen. Elect. Rev. 237 (1922).
[9] C. Ramsauer, Ann. d. Physik **64**, 513 (1921).
[10] G. Hertz, Verh. d. D. Phys. Ges. **19**, 268 (1917).

principles of ordinary mechanics. K. T. Compton[11] gives this calculation. If f is the average fractional loss of energy per impact averaged over all angles, then

$$f=m/M \tag{4}$$

where m is the mass of the electron and M is the mass of the helium atom. If eV_0 be the initial energy of the electron and eV_s its energy after Z impacts then it follows that

$$V_s=V_0(1-f)^s \tag{5}$$

If we consider an electron that has 19.87 volts of energy or 0.1 volt more than it needs to cause resonance in helium we find that it can make 18.3 elastic impacts before its energy is reduced to 19.77 volts. This value for the total number of elastic impacts per 0.1 volt loss in energy is nearly constant in the range between 19.77 and 20.57 volts.

Let us consider a 19.87 volt electron just entering the second condenser. While it will make n impacts in crossing the total distance of the second condenser, we see that after the first 18.3 impacts its energy is reduced to 19.77 volts. During the remaining $n-18.3$ impacts this electron will still make before leaving the second condenser, its energy is less than 19.77 volts. None of these impacts can therefore be inelastic, and they must not be counted in our calculation of efficiency. We shall therefore calculate the total number of impacts from mechanics by means of Eq. (5).[12]

13. *The efficient impacts from the Franck Method.* We next calculate the fractional drop in current (in the Franck method) from the experimental curves (Fig. 2-*B* and *C* of the previous paper) at a point 0.8 volt beyond the beginning of the current drop. A larger range of accelerating voltage cannot be investigated because a second resonance point occurs in helium 0.8 volt higher than the first critical potential. The values obtained for the fractional current drop $\Delta D_s/D_0$ are given in Table IV, column 5. From the variation in individual experiments it is seen that extrapolation of D_0 0.8 volt beyond the beginning of the current-drop is unnecessary.

We have given the values $\Delta D_s/D_0$ obtained from the runs at low pressures where there are no impacts possible in the first and third condensers. If we take into account all the experiments performed at pressures varying from 0.8 to 13 mm, we find a trend with pressure. Sponer[2] has found a similar trend with pressure in mercury. We can eliminate this trend by extrapolating to zero pressure, and then we find for the fractional current drop the value 0.08. We may therefore accept as an approximate value

$$\Delta D_s/D_0=0.1 \tag{6}$$

This ratio will be used to calculate numerical values of the resonance efficiency. We are studying, however, two distinct problems. The first problem is to determine the shape of the efficiency curve as to whether or not the

[11] K. T. Compton, Phys. Rev. **22**, 333 (1923).

[12] H. B. Wahlin, Phys. Rev. **27**, 595 (1926) finds from his experiments on mobilities in helium that λ is 8.6 times greater than the value calculated from mechanics. If we use Wahlin's value for λ the numerical value of the efficiency calculated in this paper would be changed.

efficiency increases to a maximum at some voltage beyond 19.77 volts and then decreases again, or whether the efficiency is constant after the energy of resonance has been reached. These questions can be answered from the similarity in shape of the electron distribution curves and the Franck-Lenard curve and the value of the ratio $\Delta D_s/D_0$ does not enter into these considerations. Only when we wish to give actual numerical values to the efficiencies do we need to use this ratio.

TABLE IV. *Values of* $(\Delta D)_s/D_0$ *for various pressures.*

Pressure (mm)	Retarding volts 3rd condenser	D_0	D_s	$\frac{D_0-D_s}{D_0}$
0.75	0	19.00	18.32	0.036
0.81	0.35	8.30	6.90	.169
0.81	0.35	6.40	5.50	.140
0.83	0.35	5.31	4.70	.115
0.83	0.35	31.45	29.35	.067
1.01	0	25.00	22.42	.103
1.83	0	22.89	19.42	.152
			Average	0.11 ± 0.04

The general scheme of analysis used in the following section is to study all conceivable shapes of efficiency curves, and to apply them to our experimental electron velocity distribution curve (Fig. 1). This procedure will give us calculated Franck-Lenard curves. These theoretical curves will then be compared with the experimental Franck-Lenard curves (Fig. 2). The particular efficiency curve which produced the best fit between experimental and calculated Franck-Lenard curve we will adopt as the true efficiency curve.

14. *Calculation of resonance efficiency.* If we assume the shape of the resonance efficiency curve and if we apply these assumed values to the electron distribution, we can calculate the Franck and Lenard distribution curves. The following notation is used: ΔD is the current drop or rise in a Franck or Lenard experiment (galvanometer deflection in arbitrary ordinates taken at tenth volt intervals); ΔG the increments or decrements in ΔD(Table II); D the total electron stream leaving the filament (galvanometer deflection in arbitrary ordinates taken every tenth volt); G the increments in D, Table I (For example $D_1=G_1$; $D_2=G_1+G_2$; $D_3=G_1+G_2+G_3$; etc.); E the average efficiency of resonance impact within a one-tenth volt interval. As the accelerating field is increased in steps of one-tenth of a volt, the first group of electrons which will have sufficient energy to cause resonance collision is G_1. They will produce the first current drop or rise in a Franck or Lenard experiment. This group G_1 will make on the average 18.3 impacts before their energy has been reduced below 19.77 volts where they can no longer make inelastic impact. A certain number of these 18.3 impacts will be inelastic because the electrons can cause inelastic impact in this energy range with an efficiency E_1. Therefore

$$\Delta D_1=ZE_1G_1 \tag{7}$$

If we increase the accelerating field another step of one-tenth volt, then the group G_2 of electrons can make inelastic impact in the same manner as the group G_1 per (7). However, the group G_1 can now produce inelastic impact in two ways. It can make 18.3 impact while its energy is reduced from 19.97 to 19.87 volts and if the average efficiency of resonance collision in this voltage interval is E_2 then, the total number of inelastic collisions will produce a change in current

$$\Delta D_2 = Z[G_1E_2 + G_1E_1 + G_2E_1] \tag{8}$$

and similarily

$$\Delta D_3 = Z[G_1E_3 + G_1E_2 + G_1E_1 + G_2E_2 + G_2E_1 + G_3E_1] \tag{9}$$

Subtracting these equations we shall have expressions for the ordinates at one-tenth volt intervals of the distribution curves of the Franck or Lenard type.

$$\Delta G_1 = Z[E_1G_1]\ ;\quad \Delta G_2 = Z[G_1E_2 + G_2E_1]\ ;\quad \Delta G_3 = Z[G_1E_3 + G_2E_2 + G_3E_1]\ ;\quad \text{etc.} \tag{10}$$

We have studied these equations by assuming various values for the efficiency and using the electron velocity distribution (last column Table I) we have constructed the theoretical Franck-Lenard curves. Of the many cases studied the following are of interest:

Case 1. $E_1 \neq 0$; $E_2 = E_3 = E_n = 0$. We assume that electrons can make inelastic impact only in the first one-tenth volt interval after 19.77 volts and that for larger energies the efficiency for resonance is zero. The Eqs. (10) then become:

$$\Delta G_1 = ZE_1G_1\ ;\qquad \Delta G_2 = ZE_1G_2\ ;\qquad \Delta G_3 = ZE_1G_3\ ;\quad \text{etc.} \tag{11}$$

It is seen that *the ΔG-curve would coincide with the G-curve if plotted on an appropriate scale.* If we should then find that the Franck-Lenard difference curves would coincide with the electron-velocity distribution curves, then we would interpret that fact to mean that the efficiency of resonance would have the values assumed above.

Case 2. $E_2 \neq 0$; $E_1 = E_3 = E_n =$ zero. We assume that electrons can only make inelastic impact in the second one-tenth volt interval after 19.77 volts and that in the other intervals the efficiency is zero. Then Eqs. (10) become:

$$\Delta G_1 = 0\ ;\quad \Delta G_2 = ZE_2G_1\ ;\quad \Delta G_3 = ZE_2G_2. \tag{12}$$

Again we find that the ΔG-curve and the G-curve would coincide if plotted on an appropriate scale. However, in order to cause coincidence of these curves, they must be shifted one-tenth volt along the abscissa. From the study of similar cases where always one of the efficiencies had a real value while the others were zero, we derived the following relation:

$$V_m = d + 0.05 \tag{13}$$

where V_m is the abscissa in volts beyond the resonance potential of 19.77 volts where the efficiency is a maximum and d is the displacement in the Franck-Lenard and electron-velocity distribution curves. We therefore interpret the fact that the experimentally determined value of the resonance potential has been found above (Table III) to lie 0.13 volts higher than the

spectroscopic value, to mean that *the maximum efficiency lies 0.18 volts above 19.77 volts.*

Since the average Franck-Lenard curve and the electron-velocity distribution curve do not exactly coincide as is seen from Fig. 3, we have studied various other cases with the efficiency maximum at 0.18 volt above 19.77 volts. The following case represents the experimental Franck-Lenard curves the best:

Case 3. $E_1=0.0011; E_2=0.0022; E_3=0.0022; E_4=0.0007; E_5=E_6=E_n=0$. The shape of Franck-Lenard curve obtained by applying this set of efficiencies to our electron-velocity distribution curve does not depend upon these particular values of the efficiencies. Any set of values which, however, must have relative magnitude as indicated will of course produce the desired shape in the Franck-Lenard curve, since we can always plot to the same scale or reduce calculated values by the use of a multiplying factor to the arbitrary chosen maximum (2.68). Table V shows the experimental and calculated Franck-Lenard curves. According to the result of section 13, the drop in

TABLE V. *Comparison of experimental and calculated Franck-Lenard curves*

Interval n	Velocity Distribution ΔG_n	Franck-Lenard Curve ΔG_n (exp.)	Franck-Lenard Curve ΔG_n (calc. case 3)
1	0.08	0.07	0.07
2	0.15	0.23	0.23
3	0.30	0.50	0.45
4	0.75	0.96	0.92
5	1.52	1.60	1.70
6	2.31	2.32	2.42
7	2.68	2.68	2.68
8	2.20	2.34	2.37
9	1.21	1.67	1.68
10	0.76	1.09	1.06
11	0.48	0.68	0.65
12	0.25	—	0.35
13	0.12	—	—

current in a Franck curve 0.8 volt beyond the beginning of the drop should be 10 percent of the total electron stream. The first eight intervals of the electron stream ($^8_1\sum G_n$) amount to ten units of current on the arbitrary scale chosen. The first eight intervals of the Franck curve ($^8_1\sum \Delta G_n$) should count unit current on the same scale. We need only reduce the ordinate actually used to plot the Franck-Lenard curve by a factor of ten to conform to the result of section 13.

The values of the efficiencies used in Case 3 above and shown in Table V give a Franck-Lenard curve whose ordinates are one-tenth as large as the electron-velocity-distribution curve. The efficiency curve which is used to obtain the best fit of the Franck-Lenard curve is shown in Fig. 4.

Case 4. $E_1=0.001; E_2=0.002; E_3=0.002; E_4=0.001; E_5=0.0006; E_6=E_7=E_n=0.0004$. This case differs from the preceding case only in that the efficiencies from E_5 to E_n have been given values different from zero. It is

seen that the resulting Franck-Lenard curve does not fit the experimental electron velocity distribution curve as well as in Case 3. We therefore believe that the efficiency of resonance *decreases rapidly beyond the maximum to a very small value.*

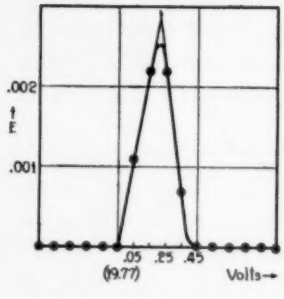

Fig. 4. Efficiency of resonance as a function of electron energy.

Case 5. $E_1=E_2=E_n=$constant. The types of efficiency curve studied in the cases cited so far had a maximum at some point beyond 19.77 volts and they decreased rapidly beyond the maximum. We investigated the possibility that the efficiency might not be small beyond the maximum. The resultant Franck-Lenard curves do not fit the experimental distribution curve at all. The extreme case studied is the case of constant efficiency throughout the voltage range. The Eqs. (10) then become:

$$\Delta G_1=ZED_1\,;\quad \Delta G_2=ZED_2\,;\quad \Delta G_3=ZED_3 \tag{14}$$

The Franck-Lenard curve resulting from the assumption of constant efficiency shows no maximum and it is evident that our experimental data do not fit such a case at all.

The cases of especial interest are shown in Fig. 5. The type of efficiency curve studied is shown in the upper portion of the figure and the calculated Franck-Lenard curves obtained by applying the respective efficiency curves

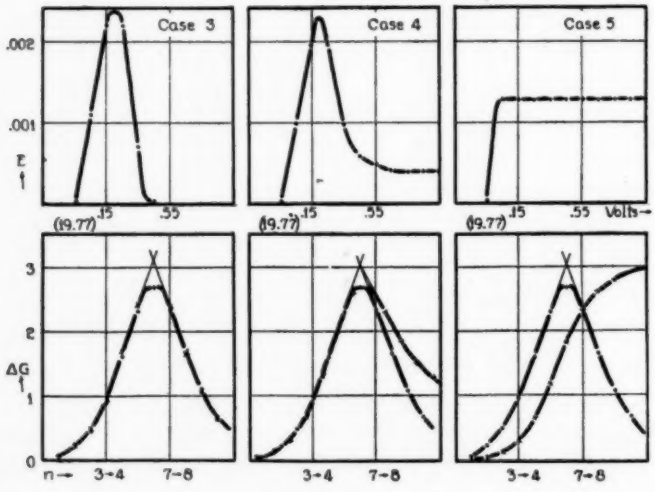

Fig. 5. Assumed efficiency curves and the resulting Franck-Lenard curves.

to the experimental electron velocity distribution curve are shown in the lower position of the figure. The calculated Franck-Lenard curves have been displaced 0.13 volt so that their maxima coincides with the maximum of the experimental Franck-Lenard curve. This coincidence could of course not be brought about in Case 5. It is evident that the efficiency curve of Case 3 shown in Fig. 4 gives the best fit to the experimental curves.

15. *Discussion of Results.* We have established the experimental fact that the electron velocity distribution curve and the Franck-Lenard curve have very similar shapes. The efficiency of resonance as a function of electron speed has been deduced. It is shown that the maximum of the efficiency curve lies 0.18 volts beyond 19.77 volts. The efficiency curve must have a maximum as the assumption of constant efficiency beyond 19.77 volts leads to Franck-Lenard curves which do not fit the electron velocity distribution curve.

It may be thought that the displacement of 0.13 volts of the curves is not known with sufficient accuracy to warrant any deduction in regard to the efficiency. However, our measurements of critical potential have an average deviation of only 0.3 percent and it will not be an easy matter to increase the accuracy of these measurements. Our potentiometer batteries were of the small lead storage cell type and their voltages were measured in terms of a standard cell before and after each run and they never changed more than a few hundredths of a volt during a run. We considered the possibility that the current flowing across the first condenser might vitiate the potentiometer principle but from the known sensitivity of our galvanometer we found that the current involved could have no effect on the voltage as calculated from the resistances of the potentiometer.

Even if the details of our efficiency curve are not accepted, certainly our experiments do support the statement: *electrons of energy somewhat larger than 19.77 volts make inelastic impact with greater efficiency than do electrons with larger velocities.*

If we accept the situation that the maximum of the efficiency curve lies about 0.2 volt beyond 19.77 volts and if we consider that we have found (previous paper) that the difference between the first and second transition in helium is 0.74 volts it would seem to follow that the second transition must have its maximum efficiency about 0.15 volts beyond 20.55 volts. It may seem surprising that critical potential measurements made so far have checked with spectroscopic data but the accuracy of the former measurements has never been sufficiently high to take into account or discover differences of the order of one-tenth of a volt. There exists no *a priori* reason to believe that the two transitions studied should have the maxima of their efficiency curves displaced the same volt amount above their respective critical potentials and we must at present simply accept the situation as an empirical fact.

It is of interest to summarize the arguments that support a relation between efficiency and electron energy of the type shown in Fig. 4. (1) The relative intensity of the ortho and para-helium spectrum as observed by Runge and Paschen[13] depends on the relation between field strength and pressure. At high pressures the ortho-helium spectrum predominates since the resonance potential for the transition to ortho-helium is less than the first resonance potential of para-helium. At low pressures the para-helium spectrum is the more intense. (2) One single correction of the volt scale brings all the critical points of a current-potential curve into agreement with

[13] Runge and Paschen, K. Preuss. Akad. Wiss. Berlin 323, 377 (1895).

spectroscopy.[14] (3) The slope of a photoelectric current potential curve is largest at the beginning of the curve and then decreases.[1] (4) The distribution curve of the current drop in a Franck experiment and of the current rise in a Lenard experiment follows the distribution curve of the impinging electrons, (our own experiments outlined in this paper).

If we compare our results with the results of Dymond[3] we see that in both sets of experiments the efficiency shows a maximum very near the resonance potential. It is evident from the foregoing considerations that the complications in the analysis are all due to the fact that electrons from the filament have a velocity distribution and in order to obtain better agreement in such experiments by different methods it will be necessary for more exact measurements to use a velocity filter in order to produce a homogeneous electron stream.

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MINNEAPOLIS, MINNESOTA.

[14] Franck and Jordan, Handbuck der Physik. Julius Springer, Berlin 1926. Page 723.

THE EXISTENCE OF METASTABLE MOLECULES IN ACTIVE NITROGEN

By Joseph Kaplan

Abstract

It has been shown in the present experiments that active nitrogen contains, among other things, metastable molecules of nitrogen possessing about 8 volts energy. The evidence that is presented to prove this statement is the excitation of the fourth positive group of nitrogen simultanesously with the quenching of the afterglow by a mild electric discharge. The main spectroscopic characteristics of a condensed discharge have been reproduced by simply introducing active nitrogen into a weak discharge. The relation of these phenomena to the structure of the nitrogen molecule is discussed.

SUGGESTIONS that the characteristics of the afterglow in active nitrogen could be wholly or partially explained by the existence of metastable molecules of nitrogen possessing about eight volts energy, have been made by Saha and Sur,[1] Birge,[2] Kaplan and Cario[3] and others. The only basis for the existence of metastable nitrogen molecules was for a long time the fact that one could offer them as an explanation of the nitrogen afterglow. Recently however as a result of the study of the electronic states in molecules by Hund, Mulliken,[4] and Birge and from the study of the spectrum of nitrogen in the far ultra-violet by Sponer,[5] independent reasons have been found for postulating the existence of metastable nitrogen molecules.

The most recent assignment of electronic states by Mulliken calls the X or normal level of nitrogen a ^1S level and the first electronic level at about eight volts either a ^3S or a ^3D level. One would therefore expect this level to be a metastable one because of the high improbability of a transition between a singlet and a triplet level. The absence of this transition is proved by the failure of repeated efforts to observe the bands that would arise in the transition A-X. It seems therefore that one is justified in assuming that this first level is metastable.

The purpose of the present communication is to present experimental evidence as to the existence in the afterglow of these metastable nitrogen molecules.

Active nitrogen can lose part of its afterglow when a weak discharge is passed through the glowing gas. This was first observed by Strutt.[6] Since the observation of this phenomenon very little mention has been made of it in spite of the fact that it has probably been often observed. In the present

[1] Saha and Sur, Phil. Mag. **48**, 421 (1921).
[2] Birge, Nature **114**, 642 (1924).
[3] Kaplan and Cario, Nature **121**, 906 (1928).
[4] Mulliken, Phys. Rev. **32**, 186 (1928).
[5] Sponer, Proc. Nat. Acad. Sci. **13**, 100 (1927).
[6] Strutt, Proc. Roy. Soc. **A91**, 303 (1922).

experiments attention was called to this effect purely by accident. An obvious experiment to try in the study of active nitrogen is the behavior of the gas under the action of electronic bombardment. If the active nitrogen is atomic then the atomic lines ought to be excited when a discharge is passed through it. Since an ordinary uncondensed discharge through molecular nitrogen does not excite any of the arc lines of nitrogen in the visible or near ultra-violet, it is apparent that the excitation of these lines when a mild discharge is passed through active nitrogen would be a very good indication that atomic nitrogen is present in the afterglow. Attention should however be called to the fact that a negative result in such an experiment would not be a proof that atomic nitrogen is absent. The lowest known electronic level in molecular nitrogen has an excitation potential of about eight volts. This value is lower than the energy necessary to excite any of the visible arc lines of nitrogen. It is quite possible, therefore, that in a mixture of atomic and molecular nitrogen the arc lines would be only feebly excited. The experiment was however tried in the hope that a positive result would follow.

In the present experiments active nitrogen was produced by passing a condensed discharge through streaming commercial nitrogen. The pressure was about 0.5 mm, at which pressure the production of the glowing gas was very great. Commercial nitrogen contains oxygen in amount sufficient to provide the impurity that has been found to be necessary in order that glowing active nitrogen be produced. The active gas was allowed to diffuse into another bulb through which a mild discharge could be passed. The spectra of these discharges were photographed on a small quartz Hilger spectrograph. In order to determine the effect of the presence of active nitrogen, photographs were taken both with and without the presence of active nitrogen.

In addition to the above method of producing active nitrogen, air, instead of commercial nitrogen was used in the discharge tube. Earlier experimenters invariably reported that the presence of more than about two percent oxygen was fatal to the production of the active gas. Since then, most experimenters have assumed that this was correct and no doubt with the many possible experimental conditions that can arise, the early experiments were correct. The author[7], however, was able to produce active nitrogen by passing a condensed discharge through air. The resulting afterglow which was blue in color differed spectroscopically from the better known straw yellow afterglow in that the first positive bands of nitrogen were greatly weakened because of the presence of the oxygen. Simultaneously with the author Herzberg[8] also reported the production of active nitrogen in mixtures of oxygen and nitrogen in which the percentage of oxygen was as high as that found in air.

We now go on to describe and to discuss the results of the above experiments. Before doing so, however, it may be well to state that the results were indentical for the active nitrogen produced from air and for that produced from commercial nitrogen. The most outstanding effect of a mild discharge through active nitrogen was the excitation of the fourth positive

[7] Kaplan, Proc. Nat. Acad. Sci. **14**, 258 (1928).
[8] Herzberg, Zeits. f. Physik **46**, 878 (1928).

group of bands of the nitrogen molecule. This group of bands was first observed by Strutt[9] under rather striking conditions. Strutt found that one of the main differences between a condensed and an uncondensed discharge in nitrogen was the excitation of the fourth positive group in the former. Later work showed that it originated on the highest known electronic level of the molecule. The 0–0 band in this group requires 14.8 volts for its excitation. Since, in order to obtain active nitrogen in any appreciable quantity, it is necessary to use a condensed discharge rather than an uncondensed one, this difference between the two discharges, suggested to Sponer[10] the following idea. All of the known fourth positive bands originate on the *D* level that has zero as its vibrational quantum number. Bands arising on higher *D* levels have not been observed, suggesting that the binding in this state is so weak that dissociation occurs quite readily. A discharge, in which these bands are highly excited, should therefore, according to Sponer, abound in atoms and this is cited as an argument that active nitrogen is primarily atomic nitrogen.

We can however, from the present experiments, discuss the excitation of the fourth positive group from an entirely new point of view. The result which we are going to discuss is the excitation of the fourth positive group when the afterglow is weakened by a mild discharge. It is apparent that the simplest interpretation that one can give to this phenomenon is, that when the discharge is passed through active nitrogen, there is present a modification of the nitrogen molecule which possesses more energy than the normal molecule. It is this modification, which is excited by the weak discharge to give the *D* level of the molecule. The conclusion is a reasonable one when one considers that when active nitrogen is present the *D* level is excited, whereas when active nitrogen is absent, the same discharge is unable to excite this level. The presence of a small amount of active nitrogen is sufficient to bring out strongly the fourth positive group at the same time that the afterglow itself is being weakened. In the following we will discuss the connection between these two facts.

We concluded in the last paragraph that an excited modification of the nitrogen molecule must be present in the afterglow. For several reasons the first electronic level is suspected to be the one in which the modified molecule finds itself. There are several reasons for thinking that the first or *A* electronic level is a metastable one and these have been given in the earlier part of the paper. In a paper which is to appear elsewhere, Cario and the author base an hypothesis as to the nature of active nitrogen on the presence, among other things, of these metastable nitrogen molecules in the afterglow. The results of the present experiments are proposed as experimental evidence for the presence of metastable molecules in the glow. In brief, the quenching of the glow by a mild discharge is explained as being due to the excitation of metastable molecules to higher electronic levels by the mild discharge.

[9] Strutt, Proc. Roy. Soc. **A85**, 377 (1917).

[10] Sponer, Zeits. f. Physik **34**, 622 (1925).

It was mentioned above that the active nitrogen that was used in the present experiments was formed in one of two ways and that the results were the same for both "varieties" of active nitrogen. Without discussing this point in detail it is possible to point out its significance. In the active nitrogen that is produced from air the visible afterglow is considerably weaker than in that produced from relatively pure nitrogen. The excitation of the fourth positive bands in this case however shows that metastable molecules are present in both the active nitrogen produced from air and in that produced from the commercial nitrogen and that the presence of the metastable molecules alone is not sufficient to give rise to the visible glow. This is in agreement with the recent ideas on active nitrogen presented by Cario and the writer.[3]

In addition to the excitation of the fourth positive bands, Strutt[9] observed several other differences between the condensed and the uncondensed discharges through nitrogen. The second positive group of nitrogen corresponds to transitions between the C and the B electronic levels. Strutt observed that this group was considerably enhanced in a condensed discharge, relative to the rest of the spectrum. The same result was found in the mild discharge through active nitrogen. In addition, it was noted that several of the bands were especially enhanced, i.e., the intensity distribution among the bands themselves was changed. This change in the intensity distribution among the bands could not be traced to the enhancement of any one upper level.

Strutt[9] also observed that the γ bands of nitric oxide, which are strongly excited in the uncondensed discharge, are almost completely absent from the condensed discharge. This was also found to be true for the mild discharge through active nitrogen. The phenomenon of the weakening of the α bands in the condensed discharge has of course been reproduced in the present experiments since the effect of the mild discharge is to weaken the visible afterglow.

It is worthy of note therefore that we have reproduced the main spectroscopic characteristics of a condensed discharge through nitrogen by simply passing active nitrogen into a very weak uncondensed discharge. We may therefore account for these spectroscopic characteristics of a condensed discharge by ascribing them to the presence of active nitrogen in the condensed discharge itself. In this way we have accounted for the excitation of the fourth positive bands in the condensed discharge as well as for some of the other characteristics of the discharge. The quenching of the α bands in the weak discharge as well as in the condensed discharge shows that metastable molecules play an important role in the excitation of the afterglow spectrum. One can conclude that a change in the intensity distribution of the second positive group of nitrogen should arise, if one considers the Franck-Condon[11] curves for the various electronic levels that are involved in the excitation and emission of these bands. The binding* in the upper level of these bands, the C level, is approximately the same as that of the normal level of the molecule,

[11] Condon, Phys. Rev. **28**, 1182 (1926).

* By binding we refer to the value of r_0, which increases as the binding is weakened.

the X level. On the other hand the binding in the metastable A level is considerably weaker than that in either of these other levels. Consequently, if we assume that in the condensed discharge and in the mild discharge in active nitrogen, the metastable molecules are excited by electron impact to the upper levels of the second positive group, one would expect a change in the intensity of these bands.

Considerations similar to those given above for the second positive group can be brought forward in discussing the excitation of the fourth positive group. As yet, no detailed analysis has been made of the fourth positive group. Consequently we do not know the value of ω_0 for the D level. We can however indirectly make some conclusions regarding this and in that way discuss the excitation of these bands.

The strongest band in the fourth positive group is the one corresponding to the transition D_0-B_2. The two bands next in intensity are those that arise in the D_0-B_1 and the D_0-B_3 transitions. A distribution of intensity, in which the strongest band is not the $0-0$ band, is characteristic of groups that arise in transitions between two levels in which there is a difference in binding. The binding in B level can be measured by the value of ω_0, which is 1718 cm^{-1}. Consequently the value of ω_0 in the D level must be either slightly greater than this or slightly less and there are two arguments which show that the value is slightly greater.

First, the binding in the normal level of the molecule is given by $\omega_0=2345$ cm^{-1}. If therefore, the binding in the D level were stronger than that in the B level, then it would have to be nearly equal to that in the X level and we should expect that electrons possessing the necessary energy should be able to excite these bands quite readily. Duncan,[12] who tried to excite these bands by direct electron impact, succeeded in doing so, showing therefore that the binding in the X level differs only slightly from the binding in the D level. We can conclude from this therefore that the binding in the D level must be stronger than that in the B level. Further, the fourth positive bands are degraded toward the violet and therefore the moment of inertia in the upper level must be less than that in the lower level. From the rule of Birge and Mecke, that $I_0\omega_0$ is nearly constant, it can be concluded that the binding in the D level is stronger than that in the A level. It is seen therefore that the conditions of excitation of the fourth positive group cannot be explained on the basis of the Franck-Condon curves.

It is possible however to explain the excitation of the fourth positive group in a very simple manner. One can ascribe the absence of the fourth positive group in ordinary discharges to the small number of electrons that have energy enough to excite these bands. When active nitrogen is present however, electrons of as low as 6.8 volts velocity are able to excite the fourth positive bands and the probability of exciting them is therefore much greater. The value of 6.8 volts is the difference between the energy of the nitrogen molecule in the metastable A_0 level and its energy in the D_0 level. In this

[12] Duncan, Astrophys. J. **62**, 145 (1926).

way we have accounted not only for the excitation of these bands but also for the role of metastable molecules in this process.

The effect of heat on the afterglow has been reported elsewhere.[3] An experiment similar to the one above was tried when the active nitrogen was heated. The effect of heating was to destroy the afterglow but not to destroy completely the activity of the gas. The "dark modification" of active nitrogen that remained was still able to excite the *D* lines of sodium and it is this modification through which a mild discharge was allowed to pass. It was found that when a mild discharge was passed through heated active nitrogen, there was no excitation of the fourth positive bands, showing therefore that metastable molecules were absent from the "dark" afterglow. The observation that the sodium *D* lines were excited in this dark afterglow whereas the NO bands were not excited, fits in with the above result. Elsewhere, the spectroscopy of active nitrogen will be discussed and this point will therefore not be considered here.

By photographing the afterglow both in the visible and in the ultra-violet when a mild discharge is passing through it, it was found that both the visual bands of the afterglow and the β and γ bands of nitric oxide were quenched by the discharge. Now, it is known that the β bands of NO are excited strongly only in active nitrogen. Consequently the entity, that is quenched by the mild discharge, must take part not only in the excitation of the α bands of N_2, but also in the excitation of the γ and β bands of NO. It can be concluded therefore that metastable molecules must play an important role in the nitrogen afterglow and these experiments are presented as an experimental proof of this statement.

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OSCILLATIONS IN IONIZED GASES

By Lewi Tonks and Irving Langmuir

Abstract

A simple theory of electronic and ionic oscillations in an ionized gas has been developed. *The electronic oscillations* are so rapid (ca. 10^9 cycles) that the heavier positive ions are unaffected. They have a natural frequency $\nu_e=(ne^2/\pi m)^{1/2}$ and, except for secondary factors, do not transmit energy. *The ionic oscillations* are so slow that the electron density has its equilibrium value at all times. They vary in type according to their wave-length. The oscillations of shorter wave-length are similar to the electron vibrations, approaching the natural frequency $\nu_p=\nu_e(m_e/m_p)^{1/2}$ as upper limit. The oscillations of longer wave-length are similar to sound waves, the velocity approaching the value $v=(kT_e/m_p)^{1/2}$. The transition occurs roughly (i.e. to 5% of limiting values) within a 10-fold wave-length range centering around $2(2)^{1/2}\pi\lambda_D$, λ_D being the "Debye distance." While the theory offers no explanation of the cause of the observed oscillations, the frequency range of the most rapid oscillations, namely from 300 to 1000 megacycles agrees with that predicted for the oscillations of the ultimate electrons. Another observed frequency of 50 to 60 megacycles may correspond to oscillations of the beam electrons. Frequencies from 1.5 megacycles down can be attributed to positive ion oscillations. The correlation between theory and observed oscillations is to be considered tentative until simpler experimental conditions can be attained.

IT HAS been known for some time that if a low pressure mercury arc is maintained using a hot filament as an electron source there is a wide range of conditions under which a large number of the primary electrons rapidly acquire velocites whose voltage equivalent is greater than the total drop across the tube.[1] There is a larger number of electrons which have less than the expected energy, so that as a group the primary electrons have not gained energy. But there is some mechanism which either effects a rapid interchange of energy among the primary electrons or else effects a rapid and random interchange between each primary electron and some other energy store.

Various hypotheses to explain this phenomenon have been advanced,[1] but none has appeared satisfactory. A natural supposition is that electrical oscillations in the arc cause the scattering both by subjecting the electrons to rapidly changing electronic fields and by causing potential changes on the electrodes.

Dittmer[2] obtained evidence pointing in this direction but was unable to detect the oscillations themselves. To explain the scattering it was thought that such oscillations must be of about the same amplitude as the observed scattering, namely 20 volts or more, and these should be easily observable.

Penning[3] has observed oscillations of radio frequencies in low pressure

[1] Langmuir, Phys. Rev. **26**, 585 (1925).
[2] Dittmer, Phys. Rev. **28**, 507 (1926).
[3] Penning, Nature, Aug. 28 (1926) and Physica **6**, 241 (1926).

discharges in mercury vapor under the same conditions as those that lead to electron scattering. We have undertaken a more systematic investigation of these oscillations in order to determine their nature and cause, for although their voltage-amplitude appears to be very small we believe that they play a fundamental role in high current gaseous discharges. We have found that the oscillatory behavior of the arc is extremely complicated in the types of discharge tube which we have been using. Nevertheless certain features stand out as tending to confirm the theory outlined recently by Langmuir.[4] This theory will be treated in greater detail here and some of the more definite experimental results will be given.

I. Theory

Two types of oscillation seem to be theoretically possible, first oscillations of electrons which are too rapid for the ions to follow, and second, oscillations of the ions which are so slow that the electrons continually satisfy the Boltzmann Law. The mathematical difficulties when any dimension of the disturbed region is of the same order of magnitude as the mean distance between electrons or ions are such as to force us to consider only cases where such dimensions are large compared to the inter-ionic distances. Hence "electric field," "density," etc., refer to the average value of these quantities taken throughout a volume which contains many ions and electrons but whose dimensions are considerably smaller than those of the oscillating region.

A rough idea of the magnitudes involved can be obtained from the density of ionization. Taking 10^{10} as a typical low value of electron density, the inter-electron distance is 4.6×10^{-4} cm. If all the electrons throughout a certain region are displaced this distance, the resulting field strength will be 0.028 e.s.u. or 8.3 volts per cm, and the energy density in the field will be 3.0×10^{-5} ergs cm^{-3}.

A. Plasma-electron[5] *oscillations.* When the electrons oscillate, the positive ions behave like a rigid jelly with uniform density of positive charge ne. Imbedded in this jelly and free to move there is an initially uniform electron distribution of charge density, $-ne$. Choosing an orthogonal system of coordinates, consider the portion of the plasma included between two planes each perpendicular to the x-axis. Suppose each electron between these planes to be displaced in the x-direction by a distance ξ which is independent of the y and z coordinates and is zero at each bounding plane. If the displacement ξ is a continuous function of x and $\partial\xi/\partial x$ is small compared to unity, the change in density caused by the electron displacement is

$$\delta n = n\partial\xi/\partial x \qquad (1)$$

Originally the net charge was zero, so after the displacement Poisson's equation gives

[4] Langmuir, Proc. Nat. Acad. Sci. **14**, 627 (1926).

[5] The word "plasma" will be used to designate that portion of an arc-type discharge in which the densities of ions and electrons are high but substantially equal. It embraces the whole space not occupied by "sheaths." See Footnote 4.

$$\partial E/\partial x = 4\pi e \delta n \tag{2}$$

E being the electric field strength. Eliminating δn

$$\partial E/\partial x = 4\pi n e \partial \xi/\partial x \tag{3}$$

Integrating, it is found that

$$E = 4\pi n e \xi \tag{4}$$

for the field arising from the electron displacement only, (since the neglected arbitrary constant represents a uniform external field). Eq. (4) shows immediately that the displaced electrons will oscillate about their original positions with simple harmonic motion. The force on each electron is $-Ee = m_e \ddot{\xi}$ giving

$$m_e \ddot{\xi} + 4\pi n e^2 \xi = 0 \tag{5A}$$

for the equation of motion. The frequency of oscillation is thus seen to be

$$\nu_e = (ne^2/\pi m_e)^{1/2} = 8980\, n^{1/2}. \tag{6}$$

If a spherical or cylindrical instead of a plane disturbance be postulated, the same natural period of oscillation is found, but in those cases some distortion of the oscillation will occur near the center or axis respectively unless ξ/r remains small in those regions. Oscillations of this type will be called plasma-electron oscillations.

The same result in a more general form which shows the oscillations to be independent of any symmetry restriction can be obtained from the fundamental electromagnetic equations applied to an ionized gas. The earlier treatment has been retained, however, because of its simple physical ideas and its application further on to positive ion oscillations. In Gibbs' vector notation the four necessary electromagnetic equations are

$$-(1/c)\dot{H} = \nabla \times E \qquad J = (1/4\pi)\dot{E} - nev$$

$$(4\pi/c)J = \nabla \times H \qquad -m\dot{v} = eE + (e/c)v \times H$$

For sufficiently small oscillations $v \times H$ is negligible and can be dropped. Eliminating v and J gives

$$\nabla \times \dot{H} = (1/c)\ddot{E} + (4\pi n e^2/mc)E$$

Taking the curl of the first equation, H can be eliminated, giving

$$\ddot{E} + (4\pi n e^2/m)E = -c^2 \nabla \times (\nabla \times E)$$

When the electric field arises primarily from electric charges, the portion arising from $\dot{H}$ being negligible, $\nabla \times E$ can be put equal to zero and we have

$$\ddot{E} + (4\pi n e^2/m)E = 0 \tag{5B}$$

This result has no symmetry restriction and leads to the frequency given by Eq. (6).

When $\nabla \times \boldsymbol{E}$ is not zero the complete equation in $\boldsymbol{E}$ can be multiplied by $\nabla\cdot$ (i.e. operated on with div.),[6] which causes the right member to vanish. Noting that $\nabla \cdot \boldsymbol{E} = 4\pi e \delta n$ we have,

$$\partial^2(\delta n)/\partial t^2 + (4\pi n e^2/m)\delta n = 0 \qquad (5C)$$

Hence, under all conditions, the electron density is capable of simple harmonic variation of small amplitude and of frequency 8980 $n^{1/2}$.

If we omit the $\nabla\cdot$ operation but assume that $\nabla \cdot \boldsymbol{E} = 0$ we obtain the equation

$$\ddot{\boldsymbol{E}} + (4\pi n e^2/m)\boldsymbol{E} = c^2 \nabla^2 \boldsymbol{E}$$

which J. J. Thomson has used[7] in the discussion of the electrodeless discharge. The frequency and wave-length of the corresponding plane waves are related according to the equation

$$\nu^2 = ne^2/\pi m + c^2/\lambda^2$$

Thus the lower frequency limit for long waves coincides with the plasma-electron frequency. But there is no natural frequency for these electromagnetic oscillations in an infinite medium. In any actual case, however, reflection at the walls of the discharge tube gives the possibility of the formation of standing waves so that there will be a fundamental resonance frequency and a whole series of overtones. It seems likely, however, that any such oscillation will be very highly damped because of poor reflection at the tube walls.

The density of ions and electrons in the plasma of an arc of the type used experimentally is of the order of 10^{10} cm^{-3}. Using this value for n in Eq. (6) the natural frequency of the plasma-electron oscillation is found to be 9.0×10^8 cycles per sec. The wave-length of this in air is 33 cm, a value to be compared with wave-lengths from 27 cm to 81 cm found experimentally.

To calculate a rough value for the fundamental resonance frequency of the electromagnetic waves we may assume that the diameter of the bulb, 18 cm, is one-half the wave-length. This gives

$$\nu = [(8.9\times10^8)^2 + (3\times10^{10}/36)^2]^{1/2} = 12.2\times10^8 \text{ cycles},$$

and the wave-length of this in air will be 24.6 cm, a value so near to those found experimentally that the decision as to whether some, at least, of the observed oscillations may be of this type must be reserved.

The absence of space coordinates in Eqs. (5B) and (5C) shows that there is no tendency for oscillations of this type to propagate through the plasma and their group velocity is zero. As a result one can specify the phases of the electron displacement through a certain region in such a way as to give

[6] We are indebted to Sir J. J. Thomson for this method which he outlined in a letter to one of us.

[7] J. J. Thomson, Phys. Soc. Proc. 40, 82 (1928).

the semblance of a moving wave, a wave, however, which moves continuously through a fixed region without ever progressing beyond, like the familiar rotating barber poles which appear to move steadily upward without rising.

In spite of the unreality of such a wave motion from the energy transfer point of view, it is necessary to suppose the existence of oscillations in that form if it is shown that these oscillations exhibit the Doppler Effect. An analogy will show, we think, that despite its artificiality, this wave motion is one likely to arise. For this purpose the electrons may be likened to the bobs of a set of regularly spaced identical simple pendulums suspended from a rigid ceiling. If the swing amplitudes are small so that the bobs do not collide, these bobs will exhibit the same behavior in a plane that the electrons do in space. Let these pendulums, originally at rest, be set in motion by passing a horizontal bar along beneath them in such a way as just to make contact with the bobs. The bobs so touched will then oscillate with the particular wave motion under discussion. The simplicity of the exciting means, makes it readily conceivable that the electrons are excited in an analogous way.

There are three factors not yet considered which may result in a transfer of energy by plasma-electron oscillations. First and foremost, of course, the oscillating electrons may themselves be moving in a body through the plasma, an example being the beam of electrons emitted by the hot filament in a mercury arc. Such oscillations will have a lower frequency than the oscillations of the ultimate electrons because of the lower density in the beam. As a typical example we may take the case described later of the 72.6-v. 25-m.a. arc in which the current density of primary electrons at the tube wall under the electrode was probably about 3.1×10^{-4} amps. cm^{-2}. The electron velocities were 5.1×10^{8} cm $sec.^{-1}$ so that the charge density was 6.1×10^{-13} coulombs cm^{-3} corresponding to an electron density of 3.8×10^{6}. By Eq. (6) the natural plasma-electron frequency for this density is 1.8×10^{7} $sec.^{-1}$.

Secondly, the electric field of any unsymmetrical oscillation is unlimited in extent, reaching in varying intensity throughout the discharge tube and extending outside. It may be this factor which is primarily responsible for the detection of the plasma oscillations.

Finally, if a local oscillation be traversed by fast electrons having fairly uniform speeds, the alternate acceleration and retardation or the rythmical deflection of this beam will excite neighboring portions of the plasma into oscillation.

The simple mathematical theory outlined leads to a single frequency for the electron oscillations, but there are two factors which may cause departures from this condition. The Doppler effect has already been mentioned. The other factor is that the electrons are not normally at rest but move with their random thermal velocities. Fast moving electrons completely traverse a local disturbance in a small fraction of a period and do not contribute to the density n which is effective in determining the frequency. Slow moving electrons, on the other hand, remain in the same

neighborhood for several complete oscillations and do contribute to n. The division is not definite but can be fixed roughly by assigning an effective wave-length to the disturbance and treating all those electrons which traverse that wave-length in less than one cycle as fast, the others as slow. The slow-moving electrons are then those which maintain the oscillation. Each fast-moving electron in its "impact" with the disturbance either contributes energy to it or draws energy from it.

It is seen, first, that a "fast" electron for a small (short wave-length) disturbance may be a "slow" electron for a large (long wave-length) disturbance, and second, that a "slow" electron for a high-frequency oscillation may be a "fast" electron for a lower frequency oscillation. Thus the greater the wave-length and the higher the frequency the greater the value of the distinguishing velocity, and the greater the number of slow-moving electrons. In this way the effective electron density n depends on the wave-length of the oscillation and this will give rise to a decrease of frequency with decreasing wave-length in accordance with Eq. (6). Since this decrease in frequency of itself decreases the effective density still further, there is a tendency at the smaller wave-lengths toward a kind of cumulative action which may make oscillations below a certain minimum size impossible. That this may actually occur is indicated by some calculations which we have made, but the present state of the investigation hardly warrants attempting a quantitative treatment here.

Interaction of the fast moving primary electrons with oscillations of the ultimates has already been mentioned, and of course there is also the interaction of the ultimate electrons with any oscillation of the primary electrons. In either case electrons of one type stream through an oscillation among electrons of the other type and withdraw energy from it. It is immediately evident that the shorter the wave-length the less will the interaction be. There is one very suggestive possibility that should be mentioned. It has already been pointed out that because of their lower density the beam electrons have a longer period than the ultimates. But if the wave-length and wave velocity of the oscillations have suitable values, then the frequency with which the moving beam waves strike the comparatively stationary ultimates may coincide with the higher natural period of the latter and give rise to resonance.

B. *Plasma-ion oscillations.* We are now ready to discuss the slower ionic oscillations. In this case we shall assume the same type of displacement for the ions as we did for the electrons before. We then have

$$\delta n_p = -n\partial\xi/\partial x \tag{7}$$

for the increase in ion density and (by Boltzmann's Law)

$$\delta n_e = n[\exp(eV/kT_e)-1] \tag{8}$$

for the increase in density of electrons. Poisson's equation now gives

$$\partial^2 V/\partial x^2 = -4\pi\epsilon(\delta n_p - \delta n_e) \tag{9}$$

and for the relation of motion to field we have

$$e\partial V/\partial x = -m_p\ddot{\xi} \tag{10}$$

Substituting (7) and (8) in (9) and dropping terms in V^2 and beyond under the assumption that $eV/kT_e << 1$ we have

$$\partial^2 V/\partial x^2 = 4\pi en(\partial\xi/\partial x + eV/kT_e) \tag{11}$$

Taking the derivative with respect to x twice and substituting from (10)

$$\frac{\partial^2}{\partial x^2}\left(\ddot{\xi} + \frac{4\pi ne^2}{m_p}\xi\right) - \frac{4\pi ne^2}{kT_e}\ddot{\xi} = 0 \tag{12}$$

A qualitative idea of the frequency behavior of these plasma-ion oscillations can be obtained by solving Eq. (12) for the case of an infinite train of plane parallel waves. Thus if we assume the solution $\xi = \exp[2\pi j(\nu t - x/\lambda)]$ we obtain

$$\nu = \left(\frac{ne^2}{\pi m_p + ne^2 m_p \lambda^2/kT_e}\right)^{1/2}$$

for the frequency.

When $ne^2\lambda^2/\pi kT_e$ is small compared to unity the frequency approaches a limiting value analogous to the frequency of the plasma-electron oscillations. The above condition is equivalent to the requirement that λ be small compared to $2(2\pi)^{1/2}\lambda_D$, λ_D being the distance, calculated by Debye and Hückel,[8] the reciprocal of which is like an absorption coefficient of an ionized fluid for electric forces. Thus the potential in the neighborhood of a sphere charged with q units of electricity is $q/(Kr)\exp(-r/\lambda_D)$ in an ionized fluid compared to q/Kr in a non-ionized dielectric. Now

$$\lambda_D = (kT_e/8\pi ne^2)^{1/2} = 4.90(T_e/n)^{1/2}\text{cm}.$$

so that in discharges of the intensity used in our experiments where, roughly, $n = 10^{10}$ and $T_e = 10^4$, $\lambda_D = 0.005$ cm. The distance between ions averages $n^{-1/3} = 4.6\times10^{-4}$ cm. This appears to be enough smaller than $2(2)^{1/2}\pi\lambda_D = 4.4\times10^{-2}$ cm so that without approaching the fine structure limit of the theory too closely there is still room for plasma-ion oscillations near $\nu = (ne^2/\pi m_p)^{1/2}$. For mercury ions this limit is 1/600 that calculated for the electrons. Thus where the frequency of the plasma-electron oscillations is 9.0×10^8 sec.$^{-1}$ (as calculated above), that of the limiting plasma-ion oscillation is 1.5×10^6 sec.$^{-1}$

Most of the considerations applying to plasma-electron oscillations apply also to these short-wave ion oscillations. A factor which may make the latter simpler is the lower "temperature" of the ions, especially as there seem to be good reasons for supposing that the ions do not have so much chaotic as general drift motion through the plasma.

If, on the other hand, λ is considerably larger than $2(2)^{1/2}\pi\lambda_D$, the ion oscillations lose their similarity to the electron oscillations and change over

[8] Debye and Hückel, Phys. Zeits. **24**, 185, 305 (1923).

to electric sound waves. Their group velocity becomes finite and both it and their wave velocity rapidly approach the limiting value

$$v=(kT_e/m_p)^{1/2}=3.9\times10^5(T_em_e/m_p)^{1/2}$$

In our experiments then, putting $T_e=10^4$ and $(m_e/m_p)^{1/2}=1/600$ we find $V=6.5\times10^4$ cm sec.$^{-1}$ when λ is greater than about 10^{-1} cm. Thus frequencies originating from these sound waves may extend from 6.5×10^5 per sec. down, but probably not beyond some point where the wave-length is comparable with the discharge tube dimensions.

The whole transition from the electron type of oscillation to the sound type occurs practically within a 10-fold variation of λ, for when $\lambda=2(2)^{1/2}\pi\lambda_D/(10)^{1/2}$ the value $(ne^2/\pi m_p)^{1/2}$ for ν is only in error by 5 percent and when $\lambda=2(2)^{1/2}\pi\lambda_D(10)^{1/2}$ the value $(kT_e/m_p)^{1/2}$ for v is likewise only 5 percent out.

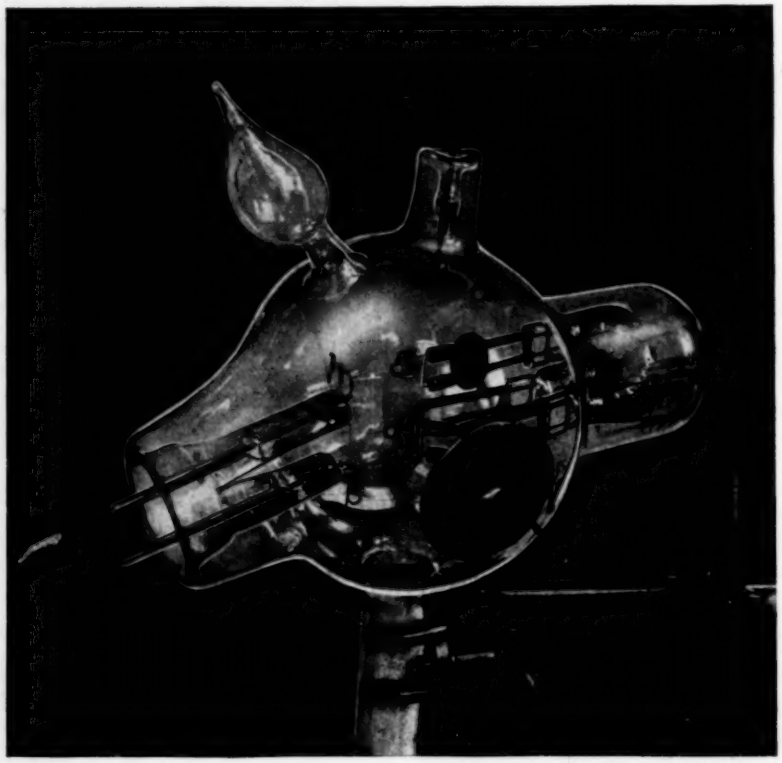

Fig. 1. Experimental tube.

J. S. Webb and L. A. Pardue[9] have described experiments in which they found oscillations that ranged from a few hundred cycles to 240 kc. in a low-pressure air discharge. As no data on the intensity of ionization and electron temperatures in their experiments are given, no quantitative comparison between this theory and their results can be made. The frequency range

[9] J. S. Webb and L. A. Pardue, Phys. Rev. **31**, 1122 (1928) and **32**, 946 (1928).

which they observed, is roughly, the range expected for the sound-like oscillations.

II. Experiments

A. Discharge tubes. On the experimental side we have worked with two tubes, both containing filamentary cathodes used as electron sources, collectors so placed as to receive a portion of the direct beam of primary electrons from a filament, and an anode off to one side to maintain the discharge. The two tungsten filaments in the first tube used were supported near the middle of the 18 cm spherical bulb by long glass-covered leads. Their exposed portions were about 1.1 cm long, parallel and about 0.5 cm apart. At a distance of 4.2 cm from them was the collector, a circular disk backed by mica and 1.1 cm in diameter. It lay in a plane parallel to that of the two filaments. An appendix containing a little mercury extended from the bottom of the bulb and was immersed in a water bath, the temperature of which controlled the mercury pressure.

The second tube was similar except that it contained three vertical tungsten filaments, *g*, *c*, and *d* in Fig. 1, *g* above, and *c* and *d* about 2.5 cm below it. These two were 0.4 cm apart and all three lay in the same plane. Their diameter was 0.025 cm and their vertical and active portions were 1.1 cm long. Opposite them and about 4 cm away were supported the 1.1 cm disk collectors *h* and *b*. The primary electrons are somewhat deflected by the magnetic field of the heating current, and the collectors are inclined as shown in order to give perpendicular incidence of the primaries on them. The glass tubes surrounding the collector leads prevented collection of ions and electrons by the back of the collector and also reduced the electrostatic capacity between leads and ionized gas. It was thought that the latter precaution might prevent a short circuiting of oscillations picked up by the collector and thus increase materially the observed amplitude of oscillation, but no marked effect of this nature is noticeable in a comparison of the results with the two tubes.

B. Detection of oscillations. The oscillations were detected with a zincite-tellurium detector and galvanometer arranged, for most of the work, in a circuit as shown in Fig. 2. The detector was supported by a spring suspension to shield it from mechanical shocks which were found to destroy its sensitivity. The high frequency potential was applied across the two points *X* and *Y*, *Y* being grounded to one side of a filament and also to the metal-screen cage surrounding the apparatus. The inductance *L* was often only a 10 to 15 cm length of copper wire. The two condensers, which were of 0.0025 μf each, shunted the galvanometer and 60-cycle crystal-calibrating circuits for the high-frequency oscillations, but at the same time allowed known 60-cycle voltages to be conveniently impressed on the crystal for calibrating purposes at frequent intervals. The impressed 60-cycle voltage in millivolts was plotted against the galvanometer deflection on log-log paper, giving a

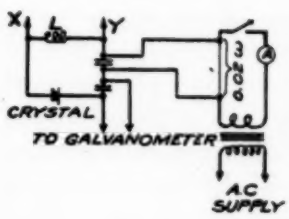

Fig. 2. Crystal detector circuit.

straight line of slope 0.5 which remained practically unchanged over considerable periods of use. This calibration was then used to interpret the galvanometer deflections arising from the gas oscillations as millivolts on the crystal. We found, however, that the same run made at different times always showed the same relative oscillation behavior but in one case the high frequency voltage might appear to be several times that in the other as if a frequency conversion factor for the crystal varied from time to time or with the crystal setting. The comparative amplitudes of a single run thus seem to be reliable, but to make more certain of comparative amplitudes in runs made at various times, high frequency as well as low frequency checking appears to be necessary.

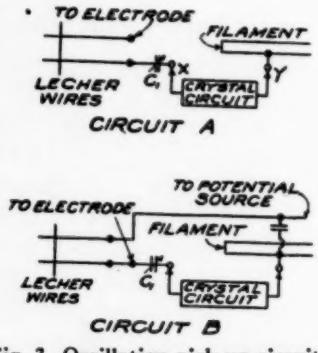

Fig. 3. Oscillation pick-up circuits.

The higher frequencies of the oscillations were determined from their wave-length as measured on a pair of Lecher wires. Circuit *B* of Fig. 3 was used to measure the oscillations of electrodes upon which it was desired to impress a voltage at the same time, while *A* was suited primarily for use with external electrodes.

C. Frequency range of oscillations. Oscillation frequencies as low as 10^6 and as high as 10^9 cycles per second have been observed. Over a large portion of this range it was not found possible to obtain any resonance phenomena, but oscillations were detected throughout so that we lean toward the view that these electric vibrations are irregular, thereby constituting an "electrical noise." Under certain conditions definite frequencies were observed both on the collectors and on external electrodes glued to the tube wall or placed against it.

The frequency range can roughly be divided into three parts, namely from 1 to 100 megacycles, from 100 to 300 megacycles, and from 300 to 1000 megacycles.

D. The range 100 to 300 megacycles. A 5 cm circular electrode (Plate I of Fig. 1) was fitted to the spherical tube wall and fastened with sealing wax so that its center was at a level about midway between the two collectors *h* and *b* and it lay opposite the space between collectors and filaments. Point *X* of the detection circuit was connected to this electrode through a variable condenser C_1 (15 $\mu\mu f$ maximum). With an emission from *d* of 25.0 m.a., an anode voltage of 62.7 and the mercury appendix at 20°C a very critical oscillation was found. Practically the whole effect lay within a range of 1.5 m.a. and 1 v. at this temperature. These oscillations did not occur when the appendix was at less than 19° or more than 21°C, the critical voltage decreasing some 5 v. in this range. The high frequency voltage at the crystal as measured was about 9 mv. The frequency was 263 megacycles at 19°C, 231 megacycles at 20°C, and 250 megacycles at 21°C, these figures probably being correct to within 2 percent.

An attempt was made to investigate the effect of additional ionization generated by emission from *g* and also the effect of the magnetic field gener-

ated by a current through c, but the results are uncertain because of the difficulty of staying on the oscillation peak. It appears that considerable emission from g (somewhere above 2 m.a.) stops the oscillations. Substitution of a smaller pick-up electrode on the tube wall and varying the setting of C_1 failed to change the frequency, but when the Circuit B of Fig. 3 was used instead of A the 230 megacycle wave disappeared and a 115-to 120-megacycle wave appeared in its place. The 230-megacycle wave was not found on the internal electrode using either circuit A or B. Reversing the filament heating current stopped the oscillations and they were not found in the similar wall position on the opposite side of the tube either when c or d was used as cathode.

The 115 megacycle wave was first found on b in the search for the 230 megacycle wave on an internal electrode. The galvanometer deflection corresponded to 30 to 50 mv. Decreasing the bath temperature from 20°C to 19.5 or less caused the oscillation peak (as the anode voltage was varied) to decrease sharply in magnitude and the frequency to jump to the neighborhood of 900 megacycles. Unlike the 230 megacycle wave, the 115 megacycle persisted over electron emissions from 22 m.a. to 35, the maximum safe current for the filament. In this range the wave-length varied from 114 to 125 megacycles. This oscillation was also found on h which was out of the direct path of the primaries from the filament, but reversing the heating current in d caused the oscillations to disappear.

At this time only the 230 megacycle oscillation had been observed on the tube wall and as it was not found on b it was thought that it might arise from some interaction between the electrons from d and the sheath about c, thus being confined to a comparatively narrow region on the wall. To explore the wall, Plate I was removed and a rectangular electrode 2.4 by 4.1 cm was arranged to slide horizontally along the surface of the tube so that its length was approximately parallel to the filaments.

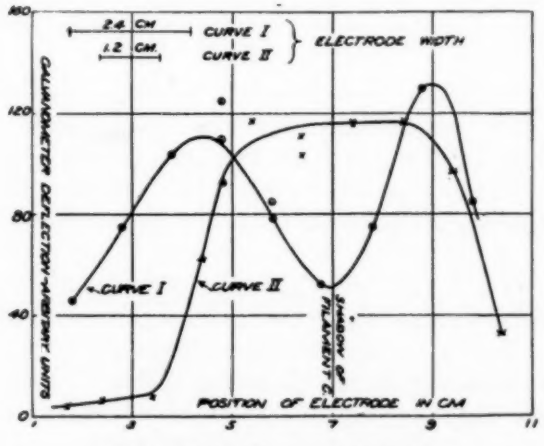

Fig. 4. Oscillations on tube wall.

It was immediately found that the oscillation present was the 115 megacycle one. Curve I of Fig. 4 shows the variation of oscillation amplitude with slider position. Another sliding electrode half as wide (1.2 cm) was then tried. The frequency of oscillation remained unchanged but the distribution on the wall showed a maximum, Curve II of Fig. 4, at the shadow where

before it had shown a minimum. The narrower electrode, having the greater resolving power undoubtedly gives the truer picture of the amplitude distribution. The minimum with the larger one must arise from a change of phase centering about the shadow of *c*. As a further test a second narrow electrode was connected in parallel with the first and as symmetrically as possible with respect to the crystal circuit. The curves of Fig. 5 show the effect of moving one while the other was fixed. The minimum followed by a rising branch as the one electrode is moved away from the other indicates that the total phase change is considerably more than 180°.

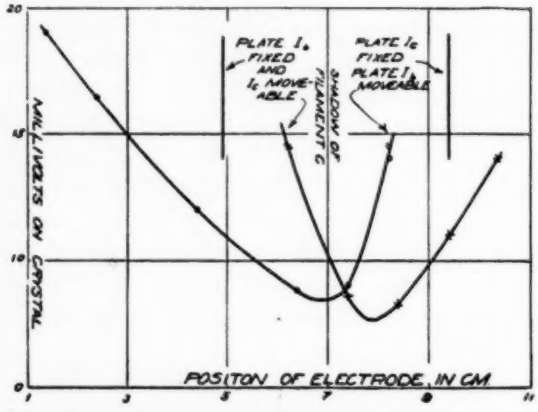

Fig. 5. Interference of oscillations on tube wall.

Apparently the presence of *c* was quite vital to the oscillations so the effect of varying its potential was tried. In the previous work it had been disconnected, its potential then being 2.5 v. positive with respect to the cathode. Fig. 6 shows the effect of varying the voltage on *c* with the 1.2 cm external electrode centered on the filament shadow. Nothing critical appears here, but the potential of *c* had a profound effect upon the localization of the oscillation, Fig. 7.

If the oscillation pattern arose from the action of *c* on the passing electrons, a magnetic field which deflected the electrons should affect the oscillation pattern equally. When tried, however, it was found that the magnetic field which had been calculated as producing a noticeable deflection caused the 115 megacycle wave to disappear and a 730 megacycle wave to appear in its place.

The frequency of 115 megacycles places that wave among the beam oscillations, but the other evidence is not clean cut. The wall pattern tends to support this point of view and the picking up of the oscillations by a collector even when it was repelling all the primaries is not in opposition to it on account of the low capacity impedance offered by the thin ion sheath to frequencies of this order. But the frequency variation with emission is too slow. A 60 percent increase in emission from 22 m.a. should, if the frequency is proportional to the square root of the electron density, cause a 26 percent increase in frequency from 114 megacycles. Actually a 10 percent increase was found, the small simultaneous voltage variation being negligible. The 230 megacycle wave may, of course, be related to the 115 megacycle as harmonic to fundamental.

E. The range above 300 megacycles. These short waves were investigated almost exclusively on the collectors although they were sometimes observed on the external electrode when conditions were not quite right for the longer and more critical oscillations already discussed. The inductance L (Fig. 2) was only that of a short length of wire shunting crystal and condensers and the arrangement of the crystal circuit in conjunction with Lecher wires and electrodes was usually that shown in Circuit B of Fig. 3.

One of the most significant features of these oscillations is that the amplitude and frequency was independent of the potential of the receiving collector over the whole range explored, namely from -80 v. with respect to the cathode to 5 v. above anode potential. Furthermore the frequency was the

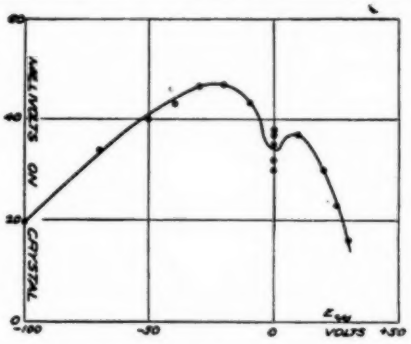

Fig. 6. Effect of potential of c on oscillations on tube wall.

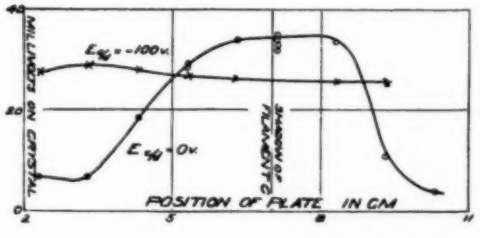

Fig. 7. Effect of potential of c on oscillations on tube wall.

same whether the primary electrons approached the collector directly, whether they were deflected past by a magnetic field, or whether a collector entirely out of the primary electron stream was used to pick them up. Reversing the heating current in the filament left both frequency and amplitude unchanged. But the situation of the filament used had some effect. With an anode potential of 33 v. and an emission of 30 m.a. a wave-length of 810 megacycles was found when g was used as cathode whereas it was 880 megacycles when d, one of the two filaments close together, was cathode.

It was natural to seek some correlation between the oscillations and the scattering of primary electrons. Unfortunately the runs meant particularly to elucidate this point are inadequate, first, because compared to the roughness of the present results the range covered was not wide enough; second, because of indeterminateness in the "temperature" of the scattered electrons, and third, because of the absence of high frequency checks on the crystal detector. But some early measurements on the first tube using a 2 m.h. coil for L in the detector circuit before any frequencies had been determined show that with 10 ma. from a 0.0125 cm filament 1 cm long the oscillations disappear in the same range of anode potential that the scattering does, namely between 60 and 75 v.

An unexpected behavior of the discharge was discovered in a certain range of current and voltage. At 20 m.a. emission with 27 v. on the anode the arc was stable in either of two conditions which were distinguished, as far as we could ascertain, only by the volt-ampere characteristic of a collector and the frequency of the oscillations. Fig. 8 shows the collector characteristic in

each state. The curves are chiefly distinguished by the degrees of scattering shown. In addition the ion currents at large negative voltages are not equal, the ions in the low scattering state preponderating by about 3 percent in this case. In other cases greater differences in the same direction were found. Transition from one state to the other could be accomplished by manipulating a bar magnet. Lowering the collector voltage caused no switch-over but raising it caused a transition from the high to the low scattering state at about 22 volts. Finally, bringing the anode to 27 v. from a high value initi-

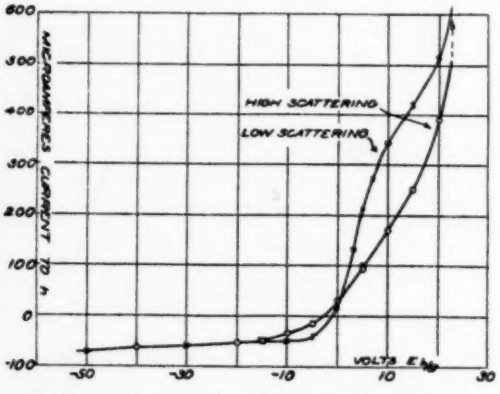

Fig. 8. Volt-ampere characteristics of a collector in the primary electron beam.

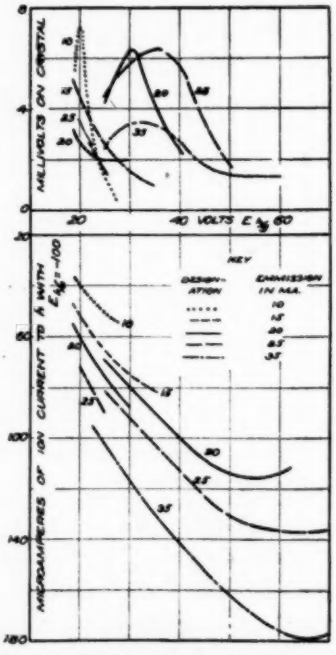

Fig. 9. Oscillation amplitudes and high- and low-scattering states.

ated the high scattering, from a low value the low scattering state. In another run, made with 30 v. on the anode several transitions occurred back and forth between the two states as the collector voltage was varied from -10 to $+20$ v. At the same time the oscillation amplitude changed abruptly, but the gaps in both sets of characteristics could readily be bridged so as to bring out the continuity of each state.

The frequency with the low scattering was almost twice that found with the high. Sometimes the arc showed less tendency to stay in one or the other state so the low scattering measurement was made with 26 v. on the anode, the high scattering with 28 v. The measured frequencies were 1080 and 660 megacycles respectively.

Fig. 9, which shows the variation of oscillation amplitude and positive ion current with anode voltage for different electron emissions, clearly exhibits the transition from the low scattering state at low emissions to the high scattering at high emissions. It is seen that at 10 and 15 m.a. only low electron scattering was found, that at 20 and 25 m.a. both low and high scattering appeared, and that 35 m.a. showed only high scattering.

The frequency of these oscillations places them among the plasma-electron oscillations. Their presence on an internal electrode irrespective of the path of the primary beam and their tendency to appear on the tube wall when other oscillations stop tend to confirm this view. The attempt was made to check them against Eq. (6), but there was no way of finding the absolute value of the ion density in the present tube because of large edge effects on the electrodes. The best we could do was to calculate relative values based on an elaborate series of measurements. Partial failure of some internal checks in these calculations show that too much reliance is not to be placed on them. Fig. 10 shows the grouping of the observed oscillations when plotted with wave-length in air against a scale of the relative ionizations. The simple theory requires that they lie in a line of slope $-1/2$. With the exception of two points out of the fifteen their deviations from the line drawn are within the accuracy of the ionization determinations. The deviations of those two may arise from some of the secondary theoretical factors.

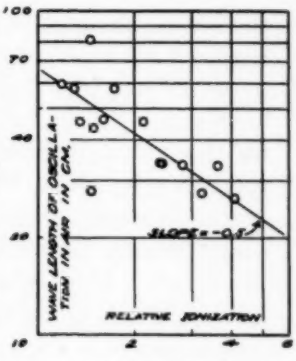

Fig. 10. Oscillation frequency and ionization density.

F. The range below 100 megacycles. While investigating the effect of Hg pressure on the 230 megacycle wave the appendix temperature was lowered to 15°C. With the emission still at 25 m.a. the oscillation maximum had apparently moved to 72.6 v. and was much less critical. Further tests showed, however, that the frequency was considerably lower than 230 megacycles and using a calibrated series tuned circuit in series with the crystal circuit it was located between 50 and 60 megacycles. At first sight it would appear possible to ascribe this frequency to the computed 18 megacycle oscillation for beam electrons together with the Doppler Effect. The frequency, ν_d, arising from the Doppler Effect is

$$\nu_d = (v_w + v_e)/\lambda$$

where v_w is the phase velocity of the waves with respect to the oscillating medium (primary electrons) and v_e is the velocity of the medium with respect to the observer. Since the beam electrons oscillate only at their natural frequency ν_e, we can replace v_w/λ by this quantity, and solving for λ find

$$\lambda = v_e/(\nu_d - \nu_e)$$

Using the values 55 and 18 megacycles for ν_d and ν_e respectively, and 5.1×10^8 cm sec.$^{-1}$ for v_e, we find λ to be 14 cm. This does not seem to be unreasonable, for it might in some way be connected with the 18 cm bulb diameter. Imagining ourselves to be travelling with the primary electrons, however, we see that each plasma electron takes $14/(5.1\times10^8) = 2.8\times10^{-8}$ sec. to traverse a wave-length. The oscillation period is only 5.5×10^{-8} sec., which taken in conjunction with the enormous preponderance of plasma electrons makes it impossible to think that these electrons do not modify the beam oscillations tremendously. In fact, a theory of infinite trains of plane oscillations as worked out by Mr. H. M. Mott-Smith, Jr. indicates that for a stationary observer the plasma-electron frequency ν_e is the minimum to be expected, the

lower frequency of the beam oscillations (as seen from the beam) being more than compensated in the Doppler effect by the shortness of wave-length required to avoid interaction with plasma electrons. Thus it seems to be impossible to identify the 55 with the theoretical 18 megacycle oscillation.

Some of the early work with an external electrode on the first tube had, we thought, indicated the presence of 15 or 20 megacycle oscillations. In searching for these Plate I was used as pick-up, C_1 was taken out of the detection circuit, Fig. 3, and a 2 mh. coil used for L. An oscillation peak of some 90 mv. was located at 25 m.a. emission and 63 v. on the anode—practically the condition for the 230 or 115 megacycle oscillation. Tuned circuits covering successive ranges from 100 megacycles down were tried in various ways in the attempt to locate the frequency. Resonance was finally established at 1.38 megacycles although considerable voltage appeared across the crystal throughout the whole range.

Between 26 and 42 v. on the anode the oscillations also reach the neighborhood of 90 mv. but the attempts to find the wave-lengths met with no particular success.

We attempted to check the 1.38 megacycle wave by using a tuned radio amplifier. For this purpose a Radiola 17 having the range 550 to 1450 kc. was set up in the cage and an antenna wire was bought near Plate I. Unfortunately the 1380 kc. wave had become so elusive that even the previous measurements of its wave-length could not be repeated so we were unable to check this. At this time the amplifier gave a noise maximum in the middle of its scale. This was not sharp, the noise extending over most of the range. Slight changes in the tube conditions caused large differences in the way the amplifier responded, sometimes several sharp noise peaks appearing, at others a single peak, and at still others only a very dull maximum. This, it seems to us, shows conclusively that there is often "a continuous spectrum" of electric oscillations in this long wave range.

The strong critical oscillation at 1380 kc. lies in the neighborhood of the theoretical short-wave limit at 1500 kc. calculated above. Whether this was actually the short-wave limit is not known, for frequencies higher than this were not sought with an amplifier.

G. Future experiments. The experiments described are in general accord with the theory outlined. A closer checking and further development of the theory, particularly with respect to the cause and critical nature of some of the oscillations, await experiments under essentially simpler conditions. With this in view we are continuing the experiments with a cylindrical tube containing a cylindrical collector at the tube wall and an axial filament. The ionization can be controlled independently of these electrodes by a hot cathode and an anode at the two ends of the tube.

In addition to Sir J. J. Thomson's letter which has already been mentioned, we gratefully acknowledge the aid and suggestions of Mr. H. M. Mott-Smith, Jr. in the development of the theory and of Mr. S. Sweetser in the experimental work.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.
November 20, 1928.

THE MOBILITY OF POSITIVE IONS IN FLAMES

By H. E. Banta

Abstract

Mobility of positive ions of K, Rb and Cs in the Bunsen flame.—The mobility was calculated from measured values of the current density, cathode drop of potential, and the thickness of the layer at the cathode in which the potential varies rapidly. The excess of ionization over recombination in the layer was assumed to be proportional to $(1-x/x_1)^m$, where x is the distance from the cathode, x_1 the thickness of the layer at the cathode, and m is a constant. J. J. Thomson supposed that $m=0$, and P. E. Boucher took $m=1$. The value calculated for the mobility depends on the value assumed for m. The results give, with $m=2$, a value of 1.8; with $m=3$, a value of 1.07 cm/sec. per volt/cm for the mobility. It is found that the mobility is the same for salts of Rb, Cs, and K, and that it does not depend on the concentration of the salt. A small increase of mobility with electric intensity is indicated by the results.

THE mobility of the positive ions has been measured by several physicists[1], and is now believed to be about one cm per sec for one volt per cm; but the possible error of this estimate is very large. The following paper contains an account of a series of experiments the object of which was to determine the mobility of the positive ions in a flame. The method used is similar to that quite recently employed by P. E. Boucher.[2] Boucher observed the variation of the potential near the electrode, and so obtained the thickness of the layer or sheath at the cathode in which the potential varies rapidly. Using a slightly modified form of J. J. Thomson's[3] theory of the variation of the potential in the sheath, the mobility of the positive ions can be calculated in terms of the thickness of the sheath, the current density, and the drop of potential across the sheath.

Theory

The theory of the variation of the potential between two electrodes in an ionized gas was given by J. J. Thomson. He showed that there was a central region of uniform electric intensity, with a sudden large increase of the electric intensity near both the electrodes. The theory may be deduced from his well known equation $d^2X^2/dx^2=8\pi e(1/k_1+1/k_2)(q-an_1n_2)$, where X is the electric intensity, x the distance from the surface of the positive electrode, k_1 and k_2 are the mobilities of the positive and negative ions respectively, q the number of molecules ionized per cc per sec, a the coefficient of recombination, and n_1 and n_2 the number of positive and negative ions per cc.

Let x_1 and x_2 be the thicknesses of the sheaths at the positive and negative electrodes respectively, and d the distance between the electrodes. J. J.

[1] H. A. Wilson, Phil. Trans. **216**, 63 (1915); Andrade, Phil. Mag. **23**, 865 (1912); Phil. Mag. **24**, 15 (1912).

[2] P. E. Boucher, Phys. Rev. **31**, 833 (1928).

[3] J. J. Thomson "Conduction of Electricity through Gases," Chaps III and IX.

Thomson assumed that the recombination an_1n_2 was equal to zero from $x=0$ to $x=x_1$, and from $x=d-x_2$ to $x=d$. From $x=x_1$ to $x=d-x_2$, X is constant and $d^2X^2/dx^2=0$; so $q-an_1n_2=0$. Also $dX/dx=4\pi e(n_1-n_2)=0$, and $n_1=n_2=n$, the recombination balancing the ionization.

J. J. Thomson's assumption that there is no recombination in the sheaths makes the value of $q-an_1n_2$ discontinuous at the surface of the sheaths, since he assumes $q-an_1n_2=q$ from $x=0$ to $x=x_1$ and $q-an_1n_2=0$ from $x=x_1$ to $x=d-x_2$. P. E. Boucher therefore assumed $q-an_1n_2$ is equal to $q(1-x/x_1)$ from $x=0$ to $x=x_1$, $q-an_1n_2=0$ from $x=x_1$ to $x=d-x_2$, so avoiding the discontinuity at $x=x_1$. This assumption, however, makes $(d/dx)(q-an_1n_2)$ discontinuous at $x=x_1$. It seems better, therefore, to assume $q-an_1n_2=q(1-x/x_1)^m$, where m is an unknown constant.

Thus $\int_0^{x_1}(q-an_1n_2)dx=q\int_0^{x_1}(1-x/x_1)dx=qx_1/(m+1)$. But $\int_0^{x_1}(q-an_1n_2)dx=nk_1X_0$, where X_0 is the uniform electric intensity between the sheaths. Thus $qx_1/(m+1)=nk_1X_0$. Since i, the current density, is

$$Xe(n_1k_1+n_2k_2),\quad nX_0=i/[e(k_1+k_2)],$$

and

$$qx_1/(m+1)=ik_1/[e(k_1+k_2)].$$

Thus

$$q=ik_1(m+1)/[ex_1(k_1+k_2)],$$

$$d^2X^2/dx^2=8\pi eq(1-x/x_1)^m(1/k_1+1/k_2)$$

$$=8\pi i(m+1)(1-x/x_1)^m/x_1k_2.$$

Integrating, $dX^2/dx=-8\pi i(1-x/x_1)^{m+1}/(k_2)+C_1$. At $x=x_1$, $X=X_0$, and $dX_0^2/dx=0$; so $C_1=0$. Integrating again, $X^2=8\pi ix_1(1-x/x_1)^{m+2}/[k_2(m+2)]+C_2$. At $x=x_1$, $X=X_0$, a small constant quantity. Neglecting it, $X^2=8\pi ix_1(1-x/x_1)^{m+2}/[k_2(m+2)]$.

Let V_1 be the potential drop across the sheath at the positive electrode, and V_2 the drop at the cathode. Then

$$V_1=\int_0^{x_1}Xdx=\{8\pi ix_1/[k_2(m+2)]\}^{1/2}\int_0^{x_1}(1-x/x_1)^{(m+2)/2}dx$$

$$=[2/(m+4)]\{8\pi ix_1^3/[k_2(m+2)]\}^{1/2}$$

In the same way it may be shown that

$$V_2=[2/(m+4)]\{8\pi ix_2^3/k_1(m+2)\}^{1/2}.$$

Thus, if the excess of ionization over recombination inside the sheaths can be represented by $q-an_1n_2=q(1-x/x_1)^m$, the mobility of the positive ions is proportional to ix_2^3/V_2^2, whatever the value of m. The variation of the mobility with the concentration of the salt vapor and with the nature of the metal can therefore be determined.

Apparatus and Procedure

The apparatus used is shown in Fig. 1. The flame used was of the Bunsen type, and was obtained by burning a mixture of natural gas, air, and spray

from a salt solution. The burner (*B*) consisted of 16 quartz tubes, arranged in three rows and cemented into a brass base. The air and gas were mixed in a Guoy sprayer (*S*). Air came from a compressed air supply, which gave a fairly constant pressure of 10 cm of mercury. To exclude any error that might arise from evaporation of the salt solution the air and gas were bubbled through water in large carboys (*C*). The carboys also served in smoothing out pressure irregularities.

The pressure of the natural gas was held constant by a pressure regulator (*R*) similar to that used by H. A. Wilson.[4] When the gas pressure mounted above the steady value desired, the inverted beaker (*F*) rose, and the mercury in the valve (*D*) closed the supply tube. When the pressure subsided to its normal value the supply tube was again opened. The pressure output of the

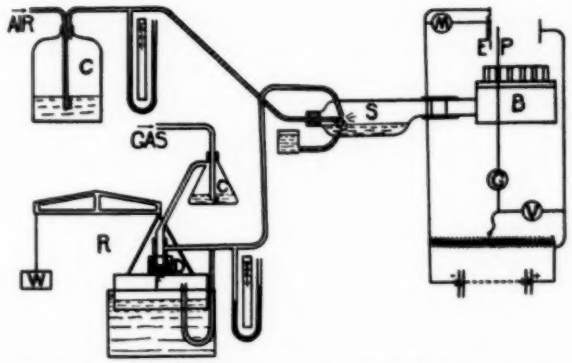

Fig. 1. Diagram of apparatus and electrical connections.

regulator was adjusted by varying a weight (*W*). The pressure used was 1 cm of water. The salt solution was introduced through a tube in the bottom of the sprayer. In this way the level of the solution inside the sprayer was kept constant.

The distribution of potential in the flame was determined by means of a very small platinum-rhodium wire (*P*), encased, except for a tip of about 0.5 mm, in a quartz tube. This tube was drawn down to a very small diameter at the tip, and was mounted on a support with an adjustable vernier scale, not shown in the diagram.

Fig. 1 shows the electrical connections. Here, *M* is a micro-ammeter, *V* a voltmeter, and *G* a high-sensitivity galvanometer shunted by a 0-50000 ohm variable resistance. The negative electrode (*E*) was a circular disk made of sheet platinum of area 1.86 sq. cm. A guard-ring of the same material shielded this electrode at sides and back, so that the current density is given by the ratio of the total current, recorded by the micro-ammeter, to the area of the front of the electrode. The other electrode was a spiral of platinum wire, about 4 cm from the first. An optical pyrometer gave the temperature of the cathode to be 1200°K, and the probe's highest temperature was 1550°K.

[4] H. A. Wilson, Phys. Rev. **3**, 375 (1914).

The experimental procedure consisted in observing the potential difference between the probe and the anode when the slider carrying the probe was set so that the probe current was zero. The probe is assumed to be at the same potential as the flame gases very near its tip. Thus, with constant potential and current between the two electrodes, the potential of the flame at any distance from the cathode could be obtained. By plotting the probe potential against its distance from the cathode, the thickness of the sheath around the cathode could be obtained. This is x_2; knowing the current and the potential at x_2, k_1 can be calculated.

Experiments

I. *Variation of the mobility with the concentration.* Solutions of KCl were sprayed into the flame, and measurements of the current, the sheath thickness, and the potential difference between the electrodes were made. The potential distribution curves for several concentrations are shown in Fig. 2. One volt

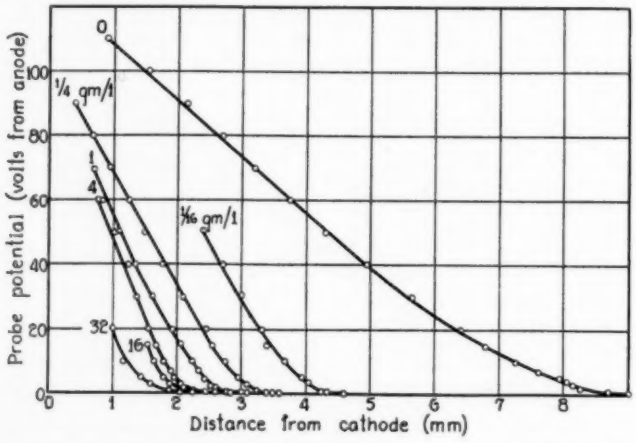

Fig. 2. Potential distribution in flame for several concentrations of KCl.

was taken as the potential at the edge of the sheath, since at about this reading the potential began to increase very rapidly as the probe approached the cathode. The results are shown in Table I; k is the solution concentration, x_2 the sheath thickness, I the total current, and V_2 the potential drop across the sheath.

Table I. *Current, sheath thickness and potential difference between electrodes for several concentrations of KCl*

k gm/l	x_2 cm	V_2 volts	$I\times10^6$ amps	$10^{12}\times Ix_2^3/V_2^2$
0	0.87	132	0.146	5.52
1/16	0.425	139	1.35	5.36
1/4	0.33	130.5	2.7	5.70
1	0.27	132	5.0	5.68
4	0.225	125	8.0	5.83
16	0.21	142	13.0	5.94
32	0.185	142	19.0	5.94

If a value be assumed for m it is possible to calculate k_1, the mobility of the positive ions, from these results. If $m=1$, $k_1=32\pi i x_2^3/(75V_2^2)$; i was taken to be the total current divided by the area of the electrode. Thus the mobility of the positive flame ions is 3.5 cm per sec. for one volt per cm (this is for distilled water sprayed into the flame). The mean of the other results, for $k=1/16$ to 32 gms per liter, gives $k_1=3.7$ cm per sec. This difference is well within the range of experimental error, as is all the variation in the mobility with the concentration.

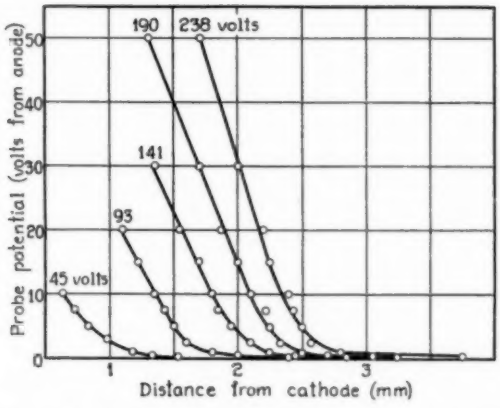

Fig. 3. Potential distribution in flame for several differences of potential between electrodes.

II. *Variation of mobility with potential.* A solution of KCl, concentration 4 gm per liter, was sprayed into the flame, and a set of readings of I, x_2, and V_2 was made for potential differences between the electrodes from 45 to 235 volts. X was obtained as has been explained previously; the potential distribution curves are shown in Fig. 3. The results are shown in Table II.

TABLE II. *Current and sheath thickness for various applied potentials in a KCl flame, concentration 4 gm/liter*

x_2 cm	V_2 volts	$I\times10^6$ amps	$10^{12}\times Ix_2^3/V_2^2$
0.13	44	4.0	4.54
0.19	92	5.7	4.62
0.24	140	7.3	5.15
0.265	188	9.7	5.11
0.29	236	12.5	5.47

In these cases the sheath thicknesses were arrived at by the shapes of the curves; and the total potential less the probe potential at the edge of the sheath was taken as V_2.

The increase of mobility with the potential is shown to be small, if it exists at all. The mobility indicated in each case can be calculated, assuming $m=1$, by the following relation: $k_1=6.4845\times10^{11}\times Ix_2^3/V_2^2$ cm per sec. for one volt per cm. I is in amps, x_2 in cms, and V_2 in volts.

III. *Variation of mobility with nature of salt sprayed.* Solutions of RbCl and CsCl were sprayed into the flame, and their mobilities compared with those obtained for KCl. The results are shown in Table III.

TABLE III. *Sheath thickness and currents for flames sprayed with CsCl and RbCl*

Salt	x_2 cm	$I\times10^6$ amps	V_2 volts	$10^{12}\times Ix_2^3/V_2^2$
CsCl	0.22	10.0	138	5.59
RbCl	0.265	5.2	139	5.08

The mean value for all the trials for KCl is about $Ix_2^3/V_2^2=5.4$; so there seems no reason to doubt that the positive flame-ions of all these salts have the same mobility.

The value of the calculated mobility depends on m thus: $k_1=32\pi ix_2^3/[(m+4)^2(m+2)V_2^2]$. Taking the mean value of Ix_2^3/V_2^2 equal to 5.4, k_1 was calculated for several values of m. The results are shown in Table IV.

TABLE IV. *Mobility of positive ions of Rb, Cs and K in flames*

m	$(m+4)^2(m+2)$	k_1(cm/sec per volt/cm)
0	32	8.2
1	75	3.5
2	144	1.8
3	245	1.07

It is seen that by taking m equal to 2 or 3, the calculated value of k_1 comes into better agreement with $k_1=1$. For either of these values of m, $q(1-x/x_1)^m=q-an_1n_2$ is continuous at $x=x_1$.

The mean value of the mobility of the positive ions of Rb, Cs, and K salts in flames is about 1.8 cms per sec. for one volt per cm, calculated for $m=2$. It is believed that the value of m is greater than one, for then troublesome discontinuities disappear, and the calculated mobility is in reasonably good agreement with the results of other investigators.

There is some indication that the mobility increases as the electric intensity increases, but the experiments give no proof of a change of mobility with the concentration of the salt.

I wish to thank Dr. H. A. Wilson for suggesting this problem, and Dr. C. W. Heaps for valuable criticisms and suggestions.

RICE INSTITUTE,
HOUSTON, TEXAS,
November 23, 1928.

ION MOBILITIES USING THE ERIKSON METHOD ON GASES OF CONTROLLED PURITY

By J. J. Mahoney

Abstract

Measurements of mobilities of ions in air and air mixed with known quantities of other gases, were made with the Erikson air-blast method under conditions in which the nature of the purity of the gas could be reasonably controlled. The results show that there is no ageing effect as observed by Erikson in air dried over P_2O_5 and liquid air, or even in air passed slowly over $CaCl_2$. In these two cases the normal positive and negative ionic mobilities are observed. If air from the room of 60 percent or 90 percent relative humidity at 20°C, is used the well-known ageing effects of Erikson are observed. With mixtures of 5 percent and 25 percent HCl no ageing effects are observed and the mobilities show the same general behavior observed by Loeb with the A. C. method. With 5 percent NH_3 the positive ion has the same mobility as the negative ion, but at ages over about 0.01 seconds both negative and positive ions show an apparent ageing, the positive ion going over to the usual value observed while the negative ion forms an ion having a mobility between the old and new positive ions. In pure C_2H_2 positive and negative mobilities were observed in agreement with those found by Loeb and Du Sault and Wahlin while in dry air with 5 percent C_2H_2 normal air mobilities were observed with no ageing effect. It is concluded that the ageing of positive ions in dry air in general proceeds very much more rapidly than Erikson assumes and possibly consists in the attachment of the initial positive ion to a bulky molecule of some impurity present. Water vapor and NH_3 inhibit this action either by forming groups which delay attachment to molecules of impurities present, or by removing the latter. Thus Erikson's ageing effects do not appear to be the true ageing but rather retarded ageing effects due to the action of water vapor or other substances.

Introduction

THE gas ion mobility determinations of Todd,[1] Wahlin,[2] Tyndall and Grindley[3] and Erikson[4,5] have shown the importance of considering the influence of the age of an ion on its mobility. Of the various methods proposed for investigating the change of mobility with age that of Erikson seems to be the simplest and enables one to operate without changing the pressure of the gas. The greatest draw-back in Erikson's method was the fact that in general he was constrained to work with either air taken directly from the room in a continuous stream or else with a continuous flow of gases from a generator or tank. The recent work of Loeb and others on mixtures has shown that the control of the purity of the gas is of great importance in the study of mobilities. In an attempt better to control the purity of the gas and to extend the mobility measurements of Erikson to mixtures of known constitution the apparatus of Erikson was modified as shown below.

[1] G. W. Todd, Phil. Mag. **25**, 163 (1913).
[2] H. B. Wahlin, Phys. Rev. **20**, 257 (1922).
[3] Tyndall and Grindley, Proc. Roy. Soc. **110A**, 341 (1926).
[4] H. A. Erikson, Phys. Rev. **28**, 372 (1926).
[5] H. A. Erikson, Phys. Rev. **30**, 339 (1927).

Description of Apparatus and Method

The arrangement of the apparatus was as shown in Fig. 1. The galvanized iron pipe containing the fan F and the condenser plates A and B could be evacuated by sealing at S and around the shaft of the motor M during exhaustion. Pure gas was then introduced, bringing the pressure in the blast pipe up to atmospheric pressure in all the gases investigated. On starting the synchronous motor M a uniform blast of gas of velocity about $1{,}270 \pm 60$ cm/sec. was forced between the condenser plates A-B. The space between the top and bottom plates of the condenser was divided into five exactly similar channels by vanes 8 mm apart as shown. On the bottom of the uppermost channel and 2 mm below the plate A was placed a very thin moveable copper plate which had been electroplated with polonium. The

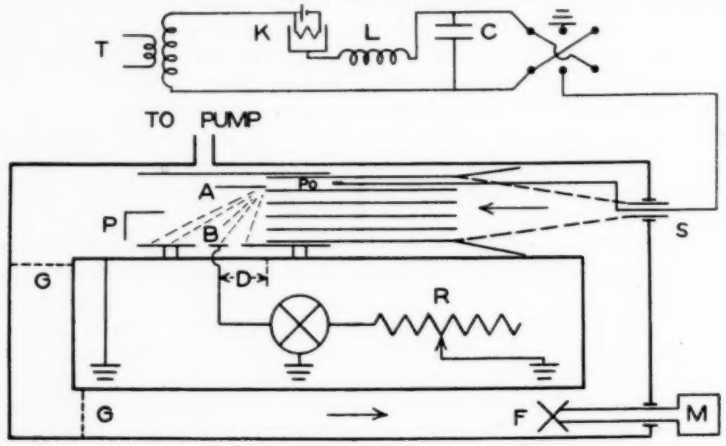

Fig. 1. Arrangement of apparatus.

vanes were each 40 cm long, thus producing a nearly uniform gas velocity at all points of the gas stream above the collector plate at D. The cross sectional dimensions of the gas blast between A and B were 5 cm wide by 3.2 cm high. On passing over the polonium some of the gas was ionized by alpha-particle bombardment. A thin layer, not exceeding 2 mm vertical dimension, of these ions was thus subjected to the force of the electric field A-B, on emergence from the ionization chamber Po. The uppermost channel containing the polonium, and the plate A were kept at the same potential. The polonium could be placed at some chosen point relative to the down-stream end of the vanes, and this point determined the age of the ion whose mobility was being measured. By moving the entire group of vanes horizontally the down-stream distance D traversed by the ions, before being caught by the electrometer collector plate, was noted. Thus, when the distances D as abscissa are plotted against the current to the electrometer, the ordinate maximum (or maxima) of the curve is at a distance D which is inversely proportional to the mobility, according to the equation derived by Erikson.[6] In a large number of his investigations Erikson used the same

[6] H. A. Erikson, Phys. Rev. **20**, 117 (1922).

method of obtaining his curves. The earthed gauzes G prevented most uncollected ions from getting back to the measuring chamber, although it is very unlikely that ions were able to pass through the 40 cm long vanes between which there was a potential gradient, due to leakage over the hard rubber sides of the condenser, without being caught.

The exact linearity of the field across these plates is questionable. If the leakage across the ebonite insulators was large compared to the irregular ionization leakage, the field should have been nearly linear. It had been intended to maintain these plates at uniform potentials relative to each other but difficulties introduced by bringing in the leads in the confined space made this inadvisable. The effect of non-linearity of the field between the plates would be most serious when the plates approached the electrometer collector plate for small values of D. In all measurements D exceeded one centimeter, and it was only within this range that evidence of irregularity was obtained as indicated by the electrometer. In most of Erikson's measurements no precautions were taken to maintain linearity of the field.

The gas velocity was found by the method of averaging, using a Pitot tube and differential inclined manometer as developed by Weeks.[7] It was found that Pitot tube readings were the same for all the gases tested except for 25 percent HCl-75 percent air (discussed in connection with Fig. 9.) This constancy of gas velocity is not surprising on considering the fact that air was the main constituent in all cases except the case of pure acetylene, and the densities of the gases employed were nearly equal. The impact pressure formula $p=1/2\ mv^2$, where p is the impact pressure of the gas, v the velocity, and m the density, gave as a velocity for all the gases (with the one exception mentioned above) 1270 cm/sec. The condenser potential (usually 3350 volts) was obtained by using a transformer T and kenetron K, and reading the potential on a Kelvin Electrostatic voltmeter. A large capacity C was in parallel with the condenser A-B. A high inductance L was in series with one side of the condenser C. These precautions were taken to obtain the constant high potential. The plate B, excepting the electrometer collector plate of dimensions 4.6 cm$\times$1.5 mm, was earthed at all times. The Cambridge type of Dolezalek electrometer, of sensitivity 320 mm per volt at one meter scale distance, was arranged to give steady readings proportional to the ionic current. This was accomplished by earthing one pair of quadrants and connecting the collecting pair of quadrants through a high resistance xylene-ethyl alcohol resistance R to earth.

The absolute value of the mobility was computed from the equation[6]

$$k=hHv/VD$$

where H is the distance between the plates A, B; V the potential difference between plates A, B; v the mass velocity of gas; k the mobility of ion; h the average distance the ions travel at right angles to the stream of air; D the downstream distance corresponding to peak of mobility curve. The mobility therefore varies inversely as the downstream distance D. Therefore

$$k_1/k_2=D_2/D_1$$

[7] W. S. Weeks, Ventilation of Mines.

The polonium was set consecutively at distances of 0, 10, 20, 30 and 40 cm from the downstream end of the ionization chamber. The ages of the ions on emergence into the field were thus approximately 0.0, 0.0075, 0.0150, 0.0225, 0.0300 seconds. The time taken for the ion to travel from *A* to *B*, assuming the negative air ion to have a mobility 2.2, and the mobility to be independent of field strength,[8,9] is about 0.0014 sec. The positive and negative ion mobilities were determined for each of the five positions of the polonium. In the graphs (except Fig. 3), the two curves at extreme left are for the ions of the least age, the age increasing in the succeeding curves.

Instrumental Contamination

By the method above outlined the gas to be studied could be introduced into the tube at the beginning of a run and the measurement could be made on the same sample of the gas for all the curves. There may have been contamination of the gas from the walls of the container and from the lubricating oil of the fan. As regards the latter, the motor was outside of the chamber and two drops of distilled Cenco pump oil were applied to the outside edge of the bearing during a week's work. The joint was sufficiently tight under these conditions so that no oil was discovered inside the chamber after a run. While filling the chamber with the given gas, the bearing of the motor shaft was made gas tight with Universal wax, which was removed as soon as the chamber was filled to atmospheric pressure, thus danger of contamination was reduced to a minimum in this respect. As regards vapors given off by the walls the problem was more difficult, particularly after the use of such reactive gases as HCl. The only recourse under these conditions was the neutralization of the gases by repeated washing with some gas which removed it, e.g., NH_3 in the case of HCl, and the evacuation to 0.1 mm or less and refilling with dry air over liquid air until normal mobilities in air had been obtained. In general, three or four repetitions of this treatment sufficed to give satisfactory results. The pumping to 0.1 mm or less on the average was, as a rule, continued for three hours using two Cenco pumps in connection with a Jones single stage mercury vapor pump through liquid air traps. Measurements were carried on in the following gases: Air dried over P_2O_5 and liquid air, air dried over $CaCl_2$ alone, undried but filtered air from room, air saturated with water vapor at about 16° C, HCl-air mixtures containing 5 percent and 25 percent HCl, 5 percent NH_3 mixed with air, and pure C_2H_2 and 5 percent acetylene and air.

Experimental Results

Dry air. The apparatus was exhausted to 0.1 mm or less and filled with dry air, re-exhausted and filled to atmospheric pressure. A series of readings was taken. These are shown in Fig. 2. The air was dried by passing over glass wool, soda lime, calcium chloride, phosphorus pentoxide and two liquid air traps in series. Contrary to the results of Erikson,[5] Tyndall and Grindley,[3] Wahlin,[2] and Nolan and Harris,[10] only one positive ion and one negative ion

[8] L. B. Loeb, Phys. Rev. **8**, 633 (1916).
[9] L. B. Loeb, Jour. Franklin Inst. **196**, 537 (1923).
[10] Nolan and Harris, Proc. Roy. Irish Acad. **36**, 31 (1922).

were found. The writer places great confidence in the above result as a set of the dry air measurements was made on at least ten samples of air. The mobilities as calculated for each of the ions in Fig. 2, are:

$$k_- = \frac{hHv}{VD} = \frac{3.1 \times 3.2 \times 1{,}270}{3{,}350 \times 1.9} = 1.98 \text{ cm/sec per volt/cm}$$

$$k_+ = \frac{hHv}{VD} = \frac{3.1 \times 3.2 \times 1{,}270}{3{,}350 \times 2.6} = 1.45 \text{ cm/sec. per volt/cm.}$$

These values were obtained from the peaks of the curves of this set and represent an average value of the mobility. The method is entirely unsuited to any accurate determination of the absolute mobility inasmuch as irregularities of the field, turbulence, and uncertainties in the true value of the average wind velocity are of such a magnitude as to make one have little confidence in the absolute numerical values. The error introduced by the effects of varying high fields on the mobility are eliminated by the method used. The *relative* values should be nearly correct for the differently aged ions in the different gases, except for whatever errors were introduced by the irregularities in the field from the plates with changing values of D. The absolute values obtained are slightly higher (10 percent) than those obtained by Erikson in such a way as to be more in accord with the new absolute mobilities in air observed by Loeb,[9] Kovarik,[11] and Tyndall and Phillips. The curves shown in Fig. 2 are those obtained on a single sample of air and coincide with all the others taken within 5 percent. The value of mobilities computed from different samples of dry air are the same within 5 percent. However, the mobility of the negative ion in dry air, with $D = 1.8$ cm, is in all cases a little greater (5 percent) than for greater values of D. This is doubtless due to the irregularities of the field between the plates mentioned before.

It is noted that the positive ion curves are distinctly broader than the negative peaks in Fig. 2, though the areas are about equal. The question arises as to whether this difference is due to an actually greater spread of the mobilities of the positive ions than of the negative ions. However, the spreading of the beam is closely correlated with the downstream distance D. To see whether a positive ion having its D equal to that of the negative ion has approximately the same width, measurements were made on the positive ions using a potential of 4,580 volts. The results may be seen in Fig. 3 in which all the curves are for positive ions, plotted under the negative ions of Fig. 2, to whose downstream distance D, they correspond. The total number of positive ions was closely equal to that of the negative ions, so that the positive curves have been slightly elongated in order to plot them to the same scale of ordinates. On the whole it is seen that the width of the positive ion peaks under these conditions are not greatly different from those of the negative ions for the same down-stream distance D. They are slightly broader at the base, an effect which possibly could be accounted for by the

[11] A. F. Kovarik, Phys. Rev. **30**, 415 (1910).

irregularities at the higher fields. It is in any case unlikely that these differences are due to any great difference in homogeneity in the nature of the positive ions, relative to the negative ions, though the slight residual differences might be accounted for on some such basis. It appears from these results that there is only one ion of each sign in the air of these measurements, after an interval of 0.0014 seconds.

Moderately dry air. Fig. 4 shows the measurements on air from the room which had slowly been passed through a meter long tube of calcium chloride. The results are analogous to those of the carefully dried air.

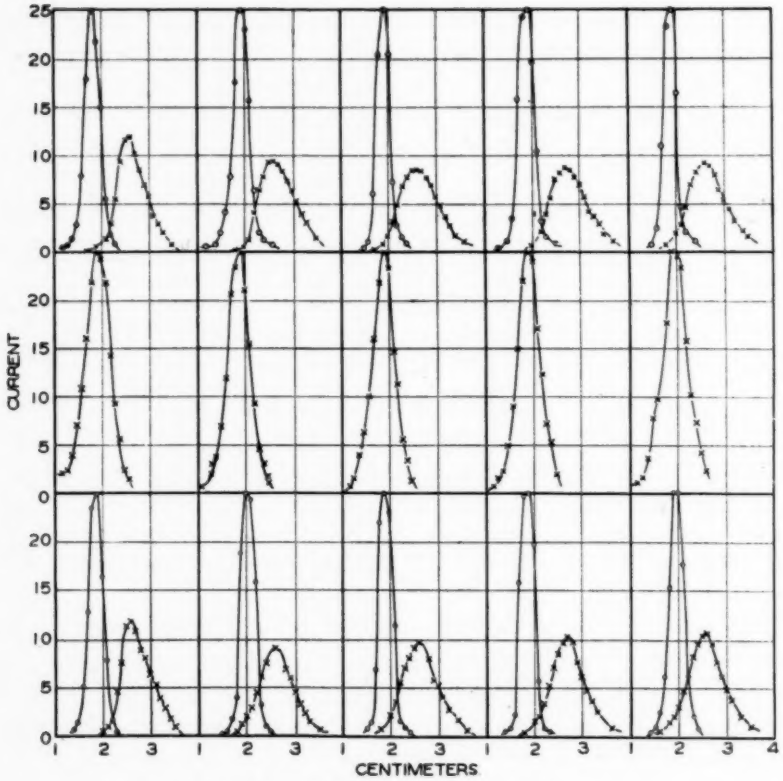

Fig. 2. Mobility curves for dry air.
Fig. 3. Showing effect of increased voltage on positive ion curve.
Fig. 4. Mobility curves for moderately dry air.

Moist air. Air from the room of relative humidity 60 percent at 20°C was introduced into the evacuated chamber. The results are shown in Fig. 5. It is seen that with this air the initial positive ion has the same mobility as the negative, in complete accord with the results of Erikson. As the ions of increased age were measured it is seen that the initial positive ion gradually changes over into a final positive ion, the negative ion remaining unchanged. In this case the mobilities of the initial negative and positive ions were 1.80, and the mobility of the final positive ion was 1.40. Erikson finds the mobility for what he terms dry air from the room to be 1.87 and 1.41, which agree

with the values in what is here termed moist air. Wahlin[2] found the time of transformation to be about 0.01 sec., while Erikson found the transformation time to the final positive ion to be 0.02 sec. Fig. 5 shows that there are nearly equal quantities of the two positive ions at an age of 0.03 sec.

Air saturated with water vapor. The air was introduced from the room after passing through a tube of cotton wool soaked in water cooled to 16°C, corresponding to a relative humidity of about 90 percent at the temperature of measurement, 20°C. It was thought advisable not to use 100 percent relative humidity as the latter would result in the deposition of water vapor on the insulation. The results for very wet air are seen in Fig. 6 and do not differ materially from Fig. 5, the mobilities for the initial ions being 1.80 and 1.4 for the aged positive ions.

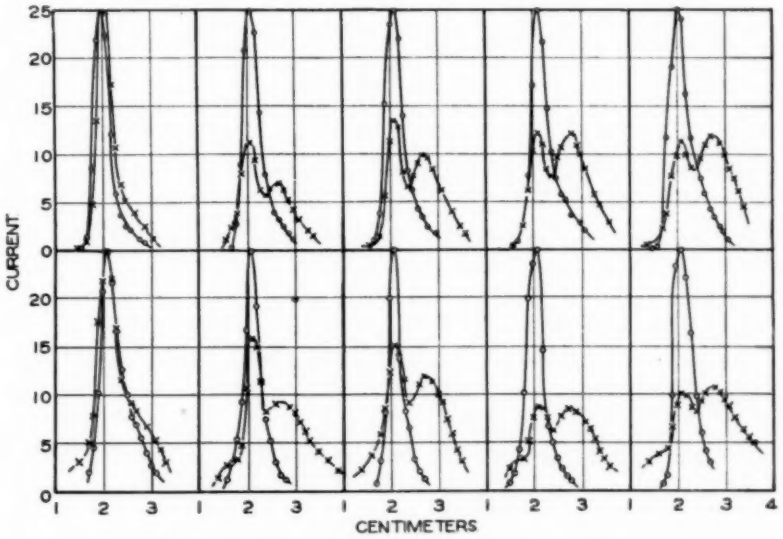

Fig. 5. Mobilities in air of 60 percent humidity.
Fig. 6. Mobilities in air of 90 percent humidity.

On comparing the widths of curves and depths of the depressions in Fig. 5 with those of Erikson[5] one may estimate that the present apparatus has a resolving power about 50 percent higher than that of Erikson's apparatus.

Effect of 5 percent ammonia. The result is shown in Fig. 7. The ammonia was obtained from a commercial cylinder supplied by the Power Specialities Co., San Francisco. It was freed of dust and dried by passing through glass wool and two liquid air traps in series cooled to −30°C, then frozen in a liquid air trap. The frozen ammonia was then allowed to evaporate into the apparatus to the requisite pressure. Air, carefully dried and purified as described for Fig. 2 was introduced, bringing the pressure to atmospheric. An analysis of the ammonia by the chemistry department showed no amines to be present. It is seen that the NH_3 caused the positive ion to acquire an increased mobility equal (within experimental error) to that of the negative.

This effect was first observed by Loeb[12] and was also reported by Erikson using this method, the values of the mobilities being 1.84 for both ions in this case. These mobilities are slightly less than for dry air. Erikson[6] found a very small peak in the positive NH_3-air curve corresponding to a mobility of the slower positive ion in moist air. The writer found an indication of a second positive peak at the same place. This peak is hardly noticeable in

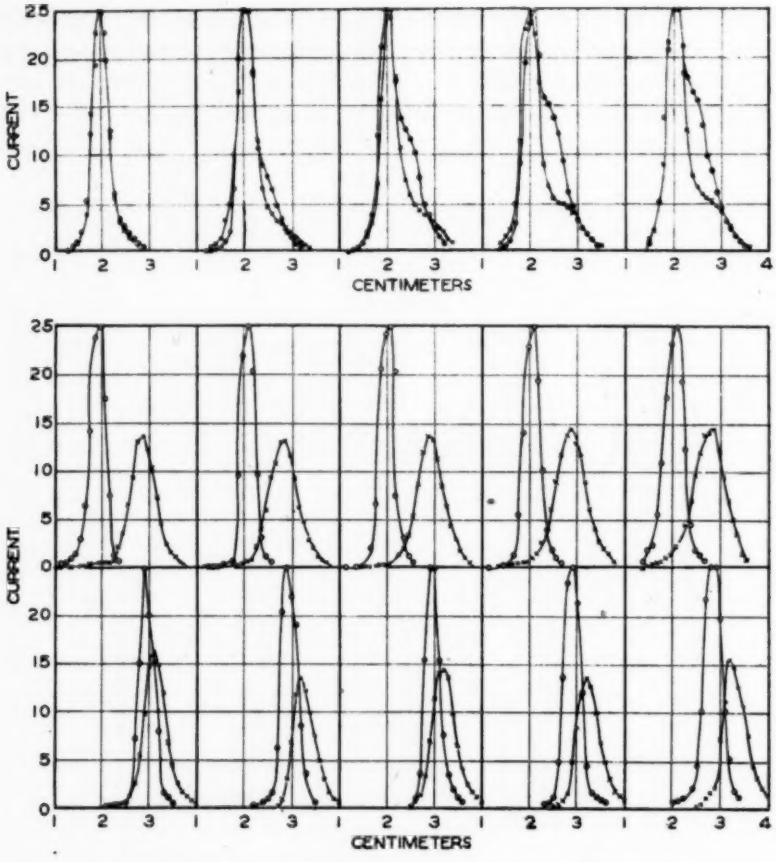

Fig. 7. Showing effect of adding 5 percent ammonia to air.
Fig. 8. Effect of adding 5 percent HCl to air.
Fig. 9. Effect of adding 25 percent HCl to air.

Fig. 7 but is very evident in the original large scale graph. Erikson could not give the quantity of ammonia used in his experiment owing to his method, thus making an exact comparison difficult. To the writer's knowledge the gradual broadening of the negative curve on the down-stream side for ions of increasing ages has never been observed before. It may indicate the formation of a negative complex of lower mobility similar to that of the positive ion in moist air, and of mobility about 1.6. Before hazarding an explanation

[12] L. B. Loeb, Proc. Nat. Acad. Sci. **12**, 677 (1926).

it is necessary to make determinations with widely varying percentages of ammonia prepared from C. P. chemicals.

Effect of 5 percent HCl. The HCl was prepared by dropping Baker's C.P. concentrated H_2SO_4 on Baker's C.P. NaCl. It was then passed through P_2O_5, through two liquid air traps in series surrounded by an ethyl alcohol bath cooled to $-75°C$, which removed the water vapor. The HCl then passed on and was frozen in a third liquid air trap from which it was evaporated into the apparatus to the requisite pressure. Fig. 8 shows the results. There was only one kind of ion of each sign. The mobility for both positive and negative ion was distinctly less than in dry air, thus showing the clustering effect of HCl as found by Loeb.[13] The mobilities are 1.8 for negative and 1.35 for positive ions while Loeb, using another method, found the values 1.6 and 1.25 respectively.

Effect of 25 percent HCl. The HCl and air in this case were introduced exactly as in the case of 5 percent HCl. The result is shown in Fig. 9. It is seen that the positive and negative ion mobilities are almost equal, the negative mobility being the higher. The values are $k_- = 1.31$, $k_+ = 1.21$. Using the Rutherford-Franck[14,15] method and with gold plated electrodes Loeb[13] found the positive and negative mobilites to be $k_- = k_+ = 1.0$. The discrepancy between the absolute values of the two results lies within the relative inaccuracy of the two methods, and might be due to contact potentials in this apparatus. Fig. 9 is not immediately comparable to Fig. 8 as the gas velocity was found to be slightly higher for the same fan speed in the case of 25 percent HCl. This was the only appreciable variation from a constant gas velocity throughout this entire series of experiments.

Effect of 5 percent acetylene. The results are shown in Fig. 10. No. C.P. calcium carbide was listed in the chemical supply catalogs. The acetylene was therefore prepared by dropping distilled water on carbide from the National Carbide Company, carbide of the highest purity obtainable. The acetylene was passed through concentrated sulfuric acid, phosphorus pentoxide, two liquid air traps cooled to $-70°C$, and then frozen in three liquid air traps in series to give sufficient gas. The solid acetylene was next allowed to evaporate into the apparatus to the requisite pressure. The additional amount of dry air necessary to bring the experimental gas to atmospheric pressure was then introduced. Only *one* negative and *one* positive ion were found. Erikson had found a positive ion of the same mobility as the negative ion, when the acetylene remained in the air only a short time before ion formation and measurement. In Erikson's[5] latest work the acetylene was allowed to remain in the air a relatively longer time and his results in the latter case were identical with those of Fig. 10. The mobilities are $k_- = 1.87$ and $k_+ = 1.35$.

Acetylene 100 percent. Fig. 10 shows the result of using acetylene prepared exactly as above. It was found that the positive and negative acetylene ions

[13] L. B. Loeb, Proc. Nat. Acad. Sci. **12**, 35–41 (1926).
[14] J. Franck, Ann. D. Physik **31**, 972 (1906).
[15] Rutherford, Proc. Camb. Phil. Soc. **XI**, (1898).

had nearly the same mobility, which looks strikingly similar to the results found by Erikson for ionized C_2H_2 measured in air, except that the value of the mobility here is much less. As the distance D of Fig. 1 could be varied only from 0 to 4.5 cm, the voltage used was increased to 5600 to make possible the measurement. The absolute mobilities were found to be $k_-=0.835$, $k_+=0.78$. These agree quite well with the results of Loeb and Du Sault[16] and Wahlin[17] using different methods.

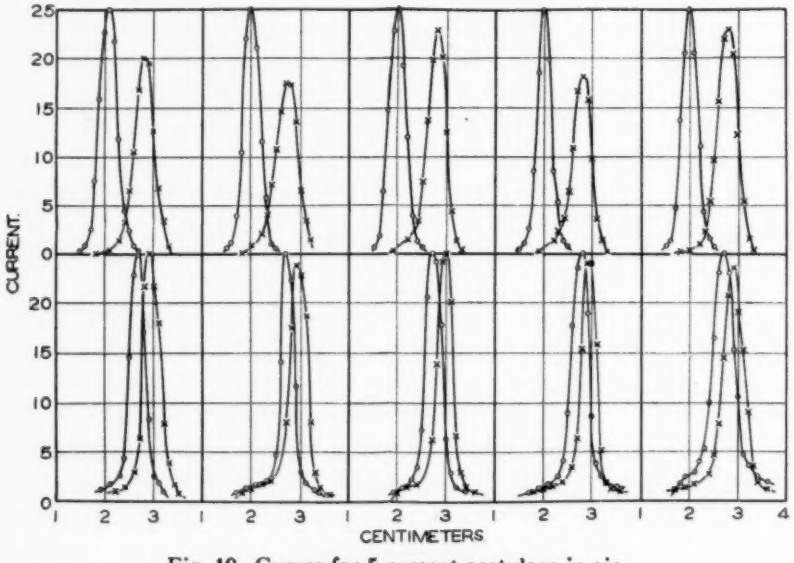

Fig. 10. Curves for 5 percent acetylene in air.
Fig. 11. Showing mobilities in pure acetylene.

Discussion of Results and Conclusions

In a recent article on the nature of gaseous ions Loeb[18] has shown from a study of mobilities in mixtures of gases that three types of behavior of the mobilities seem to occur. The first of these types occurs in mixtures of gases such as, H_2, CO_2, Air, and C_2H_2; and indicates that if the ion is a cluster it is one which does not change its constitution as the composition of the mixture is varied. The second type of behavior is exhibited by mixtures in which, while the nature of the ion is not essentially changed by the presence of one of the constituents of the mixture, the ion shows the influence of both types of gases in a way which indicates a labile or statistical[19] clustering favoring the more strongly attracted gas. This is shown by the case of the negative ion in NH_3-H_2 mixtures, SO_2-H_2 mixtures, and by the positive ions in Cl_2-O_2 mixtures. The third type of behavior can only be ascribed to the preferential clustering, or addition, of one of the gaseous constituents, even when present in small traces, to one or both ions. This occurs for the positive ion in mixtures of NH_3, ether, or SO_2 with H_2 or air; and for HCl and H_2O

[16] Loeb and Du Sault, Proc. Nat. Acad. Sci. **13**, 510 (1927).
[17] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).
[18] L. B. Loeb, Phys. Rev. **32**, 81 (1928).
[19] L. B. Loeb, Kinetic Theory of Gases, p. 472.

with air for both ions; and for Cl_2 and Br_2 in air and H_2 for negative ions. The clustering of this type depends on the chemical constitution of the gas and the sign of the charge on the ion.

One is therefore confronted with gases showing a specific cluster formation, characteristic of the gas and sign of the charge; with others where the ion is of a more labile type; and with gases where the existence of a specific cluster formation characteristic of each gas is highly doubtful. It is now of interest to see to what conclusion the ageing experiments described in this paper lead one on the basis of these facts. In HCl for both ions and NH_3 for positive ions the formation of ion complexes with traces of these gases is definitely established from the mixture studies of Loeb. In the present experiment in HCl-Air mixtures the observed mobilities indicate that the clustering effects have taken place (lowering of positive and negative mobilities in HCl and increase of positive mobility in NH_3), in a time period of less than 0.0014 seconds which is the shortest period measured in the present work. In dry air again the low mobility positive ion has formed in less than the 0.0014 seconds of the shortest timed mobility measurement. The addition of water vapor in appreciable amounts apparently produces a retarding effect on the formation of the low mobility positive ion, as does the presence of NH_3 in a much greater measure. Thus what Erikson observed and interpreted as an ageing effect was in reality an ageing effect. It was, however, not a normal one as he supposed but a retarded ageing of the positive ion due to the presence of water vapor. This gives at once a plausible reason for the difference in the rates of formation of the slow ion reported here (0.03 seconds), and those of Erikson (0.02 seconds) which may be easily ascribed to the presence of a smaller amount of the inhibiting water vapor in the case of Erikson's work than in the present case. This action of water vapor in retarding the ageing of the positive ion was first reported by Tyndall and Grindley[3] although the method which they employed was of such a nature that it did not permit of great certainty. The conclusion of Tyndall and Grindley has also been borne out by the work of Leila Valasek[20] in Erikson's laboratory using a different method. However, the striking conclusions from the present experiments which go much farther, are that ageing (and possibly cluster formation) occurs in all these gases under the experimental conditions in much shorter time intervals than usually supposed, and that the ageing observed by Erikson is not the real ageing but a retarded effect due to the action of water vapor.

As to how water vapor acts to retard ageing one can at present only conjecture. As it may stimulate further thought on the subject, one might venture to speculate to a slight extent. One may first ask to what ageing could be due. The specific electrochemical effects of certain gases on ions observed in these mixture studies enable one to hazard a reasonable supposition that in gases like CO_2, N_2, O_2 and H_2 where the dipole moments are small and large cluster aggregates are unlikely, it is possible that positive and negative ions have nearly the same mobilities. Again the presence of certain impurities in these gases which go preferentially to the positive ion forming

[20] L. M. Valasek, Phys. Rev. **29**, 542 (1927).

a stable and large group is not unlikely. When one considers that a "chemically pure" gas (less than 1 part in 10^5 of impurity) still can have 10^{14} molecules of impurity per cm^3 in it, and that an ion in a gas makes some 10^6 or 10^7 impacts in 0.001 second, the chance of picking up an impurity is relatively great. Now experiment has shown that the positive ion is exceedingly sensitive to NH_3 and still more so to ethyl ether, the latter forming a more stable and slower positive ion than NH_3. Thus it is quite justifiable to assume that the initial positive ion in air has the same mobility as the negative ion, but that in dry air* it quickly adds another bulky molecule present as an impurity and drops in mobility.

Addition of water vapor could thus conceivably act in one of two ways, by either forming an H_2O positive ion of a nature that makes picking up the larger impurity less probable, or by reducing the number of molecules of impurity by combining with such molecules to make an inactive group, e.g. with N_2O_4 to make HNO_3. Either means is equally possible. In the case of NH_3 the existence of the faster positive ion and the much decreased formation of the slow positive ions inclines one to the notion that the NH_3 complex with the positive ion acts to decrease the chance of the positive ion picking up a bulkier molecule of impurity even though the latter is more active. The field, however, needs much more quantitative study before such hypotheses can be seriously considered.

It is interesting to note that the mobilities in pure acetylene with this method agree with those of Loeb and Du Sault[16] and Wahlin.[17] It is also interesting to note that the presence of 3 percent of C_2H_2 in air does not produce the appearance of the initial positive ion as observed by Erikson[4] in an earlier paper, but yields only the aged ion with no evidence of an ageing effect. This is similar to the case of pure dry air. This is in agreement with Erikson's later work, and it is thus possible that the earlier anomalous result is a spurious one which is not a characteristic of C_2H_2.

The fact that the Erikson ageing effect is confined to moist air explains why Loeb and Cravath[18] were unable to detect this in dry air using the A.C. method. It also strengthens the suggestion made by Loeb, as Wahlin[21] in his work used dry air, that the change in mobility at low pressures for positive ions as observed by Wahlin was not in reality an ageing effect but was due to the changes produced by variation of the auxiliary fields.

In conclusion, I wish to thank Professor L. B. Loeb, at whose suggestion this problem was undertaken, for his advice and interest during the progress of the experiments.

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UNIVERSITY OF CALIFORNIA,
BERKELEY, CALIFORNIA,
August 15, 1928.

* It is possible that impurities present in the closed chamber account for the more rapid ageing than previously observed. However the presumption would be that such air is purer than that drawn from the atmosphere of a physical laboratory without drying or liquid air. Inasmuch as all previously studied gases have never been completely dried the measurements above are very significant.

TRANSMUTATION OF ELEMENTS

By L. Thomassen

Abstract

Test for the transmutation in the tungsten target of an x-ray tube.—X-ray spectrograms of the tungsten target of a deep-therapy x-ray tube were taken before and after operating it for about 80 hours at 2–3 ma and 207 kv peak voltage. No lines other than those due to tungsten were found before or after.

Test for transmutation of lead in a lead arc.—The experiments of Smits and Karssen with the lead arc were duplicated as nearly as possible. Under no conditions of current density was there any spectroscopic evidence of a transmutation of the lead to mercury.

Test for transmutation of lead in a high potential discharge between lead electrodes in CS_2.—The experiments of Smits and Karssen were carefully repeated. Some evidence of Hg in the residue from the electrodes was found. The indications are however, that the mercury comes from the electrodes, the carbon bisulphide or dust particles rather than from a transmutation of lead.

Introduction

IN RECENT years, a number of experimenters have tried to settle the important question as to whether it is possible to transmute one element into a new one by other means than α-particles. It has been maintained that light elements could be transformed by means of high potential discharges[1] and that heavy elements could be transformed in a low potential electric arc, or when subjected to high potential discharges.[2] Miethe has claimed that he was able to transmute mercury into gold, and encouraged by his results, Smits and Karssen started a series of experiments by which they thought they could prove the transmutation of lead into mercury and thallium. Miethe's work has been refuted by a number of scientists[3] while Smits and Karssens work has not been checked.

Experiments with the X-Ray Tube

If it is possible to bring about a transmutation by moderate quantities of energy, one might expect to find traces of it in an x-ray tube, where high velocity electrons impinge upon a target. If any appreciable amounts of matter were transformed, it would show up in the characteristic x-ray spectrum. The evidence one might get here would be indisputable, and as

[1] J. N. Collie and H. S. Patterson, Chem. Soc. Trans., **103**, 419 (1913); J. N. Collie H. S. Patterson and I. Masson, Proc. Roy. Soc., **A91**, 30 (1915); R. Riding and S. C. C. Baly, Proc. Roy. Soc., **A109**, 186 (1925).

[2] A. Miethe, Naturwiss., **12**, 597 (1924); A. Miethe and H. Stammreich, Zeits. f. anorg. Chem., **150**, 350 (1926); **156**, 185 (1926); H. Nagaoka, Journ. de phys., **6**, 209 (1925).

[3] E. H. Riesenfeld and W. Haase, Ber. d. D. Chem. Ges., **58**, 2828 (1925); E. Tiede, A. Schleede and F. Goldschmidt, Naturwiss., **13**, 745 (1925); E. Duhme and E. Lotz, Ber. d. D. Chem. Ges., **59**, 1649 (1926); F. Haber, J. Jaenicke and A. Matthias, Zeits. f. anorg. Chem., **153**, (1926); M. W. Garrett, Proc. Roy. Soc., **A112**, 391 (1926).

the tube remains closed all the time, the danger of accidental contamination is rather small.

Following this idea, which was suggested by Dr. R. A. Millikan, the author arranged an experiment in the following way: An unused, large, deep-therapy x-ray tube from Victor X-Ray Corporation was put at our disposal through the kindness of Dr. A. Soiland of Los Angeles. To make sure that no other lines except those of tungsten were present to start with, the characteristic K-spectrum was taken by photography, using the Bragg method. The distance between crystal and slit was the same as between the crystal and film. The crystal used was a calcite cleavage plate which was turned very slowly by means of a clockwork, a very important precaution when one does not have a very good crystal. If this is omitted, the background of the lines does not become uniform, and pseudo-lines will appear. The current was taken from a transformer and rectified by one kenetron tube. An autotransformer and resistance were used for regulation.

An exposure with 25 cm distance between crystal and film, using 83 kv and 2 ma gave a fairly good film; a new exposure under the same conditions, but with 83-85 kv gave a better film. No other lines than those of tungsten could be detected. The last exposure was taken October 16, 1925, and the tube then returned to Dr. Soiland and run by him for about 80 hours at 2–3 ma and 207 kv peak voltage. A new picture was then taken on February 3, 1926 under the same conditions as before. No lines that indicated a transmutation could be found. Later, the author had an opportunity to see a number of spectral photographs, taken with a Seeman-spectrograph of an x-ray tube that had been running for several hundred hours at around 200 kv. No foreign lines could, however, be detected.

Experiments with the Lead Arc

As the next experiment was chosen that of Smits and Karssen. They have tried out different constructions of electric arc lamps, in which lead vapor acted as the conductor, and got strong evidence of a transmutation. The results obtained are in a class by themselves for the following reasons: The transmutation products, mercury and thallium were found by photographing the spectrum of the arc, keeping the lead in the same tube in which the experiment had been performed, without touching it. The other remarkable thing is that the mercury is so abundant, and yet Smits and Karssen think that if the lamp had a long enough life, a stage would be reached, when the lead spectrum would have disappeared entirely. It is evident that these conditions made this experiment a very favorable one to repeat.

The first tube constructed by Smits was shaped like an inverted Y. Through the two legs were sealed the electrodes, and the arc was maintained across the bend. Such a tube was also constructed by the author but failed to work satisfactorily. In the meantime, Smits and Karssen had changed the construction of the lamp, and the tube which the author built and ran successfully, was as nearly as possible a copy of the tube finally used by them. The size, however, was probably smaller because of the dif-

ficulty of judging the size from their drawings and photographs. The justification for copying their tube as closely as possible is found in their statement, that small changes in the experimental conditions, may almost or entirely prevent the transmutation from taking place.

The tube used by the author was made of transparent quartz and had the following shape: (see Fig. 1.).

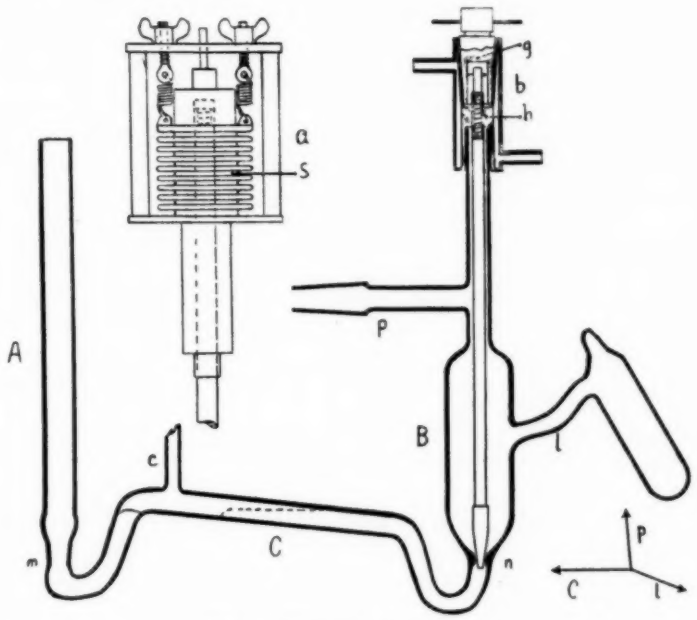

Fig. 1. Diagram of arc tube.

It consisted of two vertical legs *A* and *B*, and the connection *C*, in which the arc burned. In the two legs are inserted the rod-shaped electrodes fastened to the holder *a* (drawn separately) and *b*, which close the tube on top. The side tube *l* on *B* carries a container from which the lead used in the experiment can be poured over into the main tube. Another side tube *p* connects the lamp to the oil pump by means of a glass tube (not drawn), which is attached to the quartz tube by a cooled ground joint sealed with wax. On this glass tube are two stopcocks, the side tubes *p* and *l* are bent so that they lie in the plane of the paper; in reality they protrude as in the end view sketched on the side, where the directions of the tubes are indicated by arrows. *C* has a vertical side tube *c* which is closed by a window at the top.

The electrodes were first made of invar which was later exchanged for steel, as invar dissolves in the lead. The lower ends carry carbon points, which are turned in the shape of cones to fit the ground constrictions *m* and *n* in the quartz tube. To lift or lower the electrode in *B*, an arrangement with a cone that turns the threaded top of the electrode was constructed. The electrode holder itself is water-cooled and attached to the

tube by means of black sealing wax. This arrangement was originally used for both holders, but the strong heating of the electrode in *A* brought about some evaporation of grease from the cone. This holder was then somewhat modified, as shown separately in Fig. 1.

In Fig. 2 can be seen the tube mounted on a rectangular frame which is fastened to a heavy tripod by means of a bearing *a* and an arm *l*. This arm is excentrically connected to a pulley *b*, the axle of which is rigidly

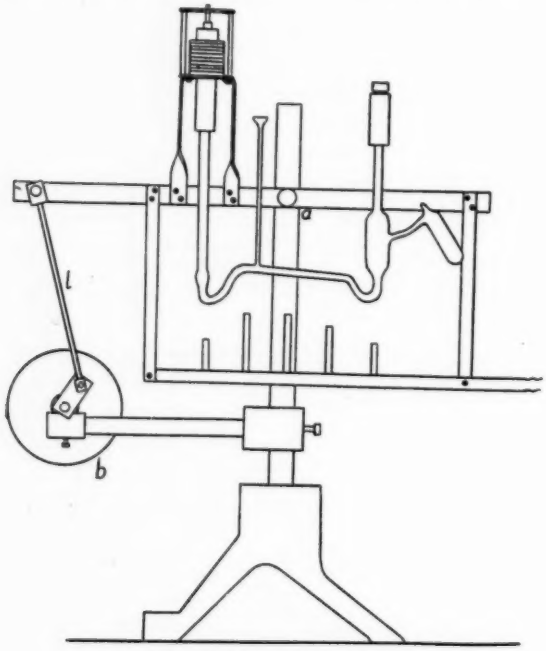

Fig. 2. Mounting of arc.

attached to the tripod. When the pulley is turned the frame is set into a rocking motion. The tube is fastened to the upper side of the frame and arranged so that it can be heated by means of 5 bunsen burners screwed on to a main tube which forms the lower side of the frame. To the frame are also fastened two copper tubes (not drawn), each having a row of fine jets directed against the quartz tube, through which compressed air could be blown to cool the tube.

For the photographing of the spectrum, a Hilger quartz spectrograph model "E 3" was used, where the spectrum from 2100 to 8000A is recorded on a 10″×4″ plate. The light is either taken out directly and by means of a quartz lens focussed on the slit, or the light coming through the window on the vertical tube *c* is reflected by means of a stainless steel mirror, and then brought to focus by the lens. Panchromatic plates from Wratten and Wainwright were used.

Great difficulties were experienced in preparing pure lead. Several methods were tried out, of which the best was found to be to recrystallize

lead nitrate, c.p., twice, heat it in a quartz tube to form lead oxide, and reduce this in the same tube by means of hydrogen. Still, this did not give lead that was free from mercury. Finally the lead was sent for, which the firm C. A. Kahlbaum in Germany had prepared for Smits and Karssen, who had found it to be almost free from mercury. The spectrum of this lead was photographed, but gave strong lines of mercury and thallium, stronger than in any of the home-made preparations. As a matter of fact, this spectrogram was used as a reference spectrogram when looking for thallium and mercury lines. The preparation of home-made lead was then resumed, and by distilling off 10–30 percent in high vacuum at 1000–1100°C the remaining lead was found to be spectroscopically free from mercury and thallium.

After the tube had been carefully cleaned, it was mounted, and the lead brought into the side tube where it was kept liquid during the whole run by means of a little electric furnace. The side tube was then sealed off, and the pumping started while the charcoal tube was heated. The further stopcock was then closed, and the charcoal cooled by liquid air. Then the frame was tipped so as to let the lead run into the main tube. The volume was regulated so that the lead filled up the tube as shown by the dotted lines in Fig. 1. A big direct current generator furnished the power, and after fastening the electric leads, so that *b* is the positive pole, the arc was started.

As has been mentioned before, the construction and the mounting of the tube are in as close agreement with the work of Smits and Karssen as could be judged at that time (fall, 1926). According to their statement, a low current density has no influence upon the spectrum, while a high current density may bring about a transmutation. They considered that they proved this by taking photographs of the spectrum before and after a run of 10 hours, at about 10 amp. No change in the lead spectrum could be observed. But by running the tube at 30–35 amp. and about 80 volts for 6 hours, the mercury lines begin to appear, and after 10 hours burning, the strongest mercury lines could be seen very clearly, and also the characteristic thallium lines. This and other experiments showed, that high current density was favorable for bringing about a transmutation, and they tried currents up to 60 amp. This was, however, rather hard on the quartz tubes. Consequently they changed their working conditions, and the construction described above is very similar to theirs. The idea is that the arc does not burn continuously, but flashes of high current density are formed when the lead surfaces are brought together by rocking the tube. At make of the arc, the current in the tube was 60–100 amp. and at the break considerably more. When this procedure is used, it is necessary to take the light out through the vertical tube, as a black film appears inside the tube that cuts down the intensity of the light. With this procedure, Smits and Karssen got strong evidence of a transmutation. After 9–1/4 hours of sparking all the mercury lines, even the very weak ones were present on the plate.

The author first made a run for 10 hours with continuous arc and low current density. The arc burns very nicely with a length of 5–7 cm at

12–14 amp. and 23–26 volts, and with some heating by the gas burners. No change in the spectrum was observed, in accordance with Smits and Karssen.

Then comes the question of running the tube with higher current densities. This means that the gas burners must be put out, and cooling applied, so as to get rid of the heat developed in the arc. But the cooling must not be too strong, because the lead must be kept liquid all the time. If it solidifies, the tube will usually break when cooling down, and invariably during reheating.

After several trials, a run of 35-1/4 hours was completed. At the make of the arc the current was 60–75 amp. for 14 hours, and 80–90 for 21-1/4 hours. Of this time about 20 percent was effective burning time for the short flashes. The amount of lead used in this experiment is only 180–200 grams, and it was found to be spectroscopically pure before the run was started. The spectra throughout the experiment were mostly photographed with 5 hour intervals under standard conditions with 12–14 amp. and 25 volts in vacuum, and showed no mercury or thallium lines. On trying to run the tube with continuous current, it broke down, because of too strong cooling.

The tube was then repaired, and a new run started with new lead, which, however, on very good spectrograms showed faint traces of mercury and thallium. Since Smits and Karssen had reported that they also had had success when the tube was filled with nitrogen, such an experiment was tried. The tube was first thoroughly evacuated and pure nitrogen let in, so that the pressure was 1/5–1/7 of an atmosphere. The length of the arc was regulated by means of cooling and heating the charcoal tube, which then took up or gave off nitrogen, and by this change in pressure, the level of the lead could be controlled.

First, an experiment with continuous current was made for 25 hours, with current densities from 15–25 amp., the latter value being maintained for 10 hours at about 38 volts. No appreciable change in the intensities of the mercury and thallium lines could be observed.

With the same tube, the method of flashing was again taken up. Accidentally it had been found, that an oscillatory motion of the lead in the short leg of the tube can be established at a certain pressure. If the two inner lead surfaces are joined, an arc is formed, which heats up and expands the nitrogen, so that the distance between the two surfaces increases very rapidly, pulling the arc out to a length of 12 cm, where it breaks. Now the nitrogen between the two lead surfaces cools off, which brings about a new contact, and a new arc is formed. These conditions were made use of in the following run, and did away with the rocking device. The pressure was again regulated by means of the charcoal tube. The actual burning time of the intermittent arc was a little less than half of the total time, and each flash lasted about half a second. After a run of 10 hours duration with a current of from 65–95 amp. at make the scheme of connections was changed, a condenser was placed across the terminals and a big inductance

in series with the tube to protect the generator against transients. With this arrangement a 12 hour run was taken the current being raised to 120 amp. in the make, but no increase in the strength of the mercury and thallium lines could be detected. On increasing the current to 150 amp., the tube broke after 2.5 hours run, but there is no doubt, that a new tube would stand that current for 5–10 hours.

As will be seen, the currents compare with and even exceed those used by Smits and Karssen, and as the diameter of the tube where the arc is burning is only 3/8″, the actual current densities are higher. On account of the smaller amount of lead used (180–200 g against ±900 g), the expected products of transmutation should be more easily detected.

Experiments with Discharges in Carbon Bisulphide

It has been mentioned before that Smits and Karssen have found that small changes in the experimental arrangements may destroy the transmutation. They have, however, also reported a second method of producing a transmutation, and they state that by this method it is possible to get *reproducible* results. The process is as follows[4] (see Fig. 3.): Two lead elec-

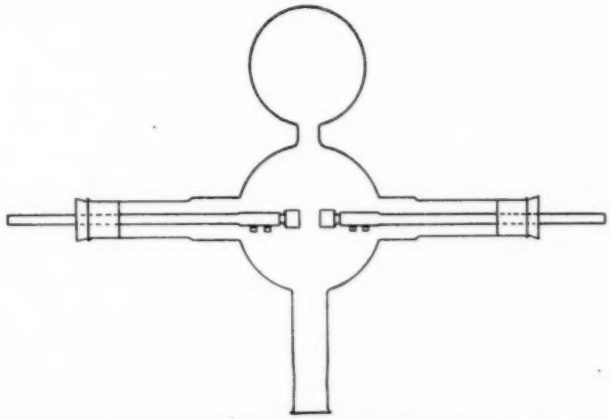

Fig. 3. Tube used for high tension discharges in CS_2.

trodes in steel holders are placed horizontally and opposite each other in a Pyrex flask. The holders are stuck through cork stoppers and are, on the other side, connected to the electric leads. The neck is closed by a stopper, through which is inserted a long glass tube, which acts as an air cooler. The flask itself is filled with carbon bisulphide. High potential discharges are passed between the lead electrodes, the surface layers of which are torn off and go out in the solution as a fine suspension which precipitates and collects in the bottom in addition to carbon and sulphur which are formed by the disintegration of carbon bisulphide. The precipitated material is collected and analyzed chemically, and mercury is found. As will be seen, this method is much less clean-cut than the previous one, as the system is

[4] Smits and Karssen, Zeits. f. Elec. Chem., **32**, 577 (1926).

not quite closed, and the mercury is found by a rather complicated chemical analysis. Another objection is that it would be very difficult to perform a reliable chemical analysis of the carbon bisulphide if one wanted to make sure that even small traces of mercury are absent. Nevertheless, the experiment was tried.

A tube like the one drawn was made, but instead of steel holders, glass tubes filled with lead were used in the first experiment. Instead of the smaller bulb underneath the main tube, a cylindrical container was used in the first experiment, similar to a test tube, in accordance with Smits and Karssen's design. Here the sputtered lead is precipitated and accumulated. The current used was taken from a set of three transformers from the Roentgen Manufacturing Co., San Francisco, one insulating transformer and two "boosters" furnished with a mechanical rectifier. Over the tube was put a screen cage for protection in case of fire.

Carbon bisulphide, quality c.p. from Baker, was used in the first experiment, after it had been dried over calcium chloride and re-distilled. In the later experiments Anchor Brand, commercially, guaranteed not less than 99.9 percent CS_2 from Wheeler, Reynolds & Stauffer, San Francisco, was used. This product was distilled once with a high rectifying column, dried over chloride and again distilled in the same apparatus. The reason for using this commerical product is a statement in the literature that mercury is sometimes used in the preparation of c.p. carbon bisulphide, which then might be contaminated with mercury. In both distillations only 4/5 of the whole volume was driven over, since there was a possibility that the heavier end-fraction might contain mercury compounds. The five percent distilling over first was also thrown away.

The runs were usually of 5–12 minutes long, separated by 20–40 minute intervals to let the carbon bisulphide cool down. In this and the following experiments the current was from 20–40 ma. The potential difference also varied considerably, but averaged 148 kv peak, measured with sphere gaps.

The first run lasted, when the intervals were added up, for 1 hour 20 minutes. The precipitated material was brought out of the tube and dried. It amounted to 7 gr, but held a fair amount of sulphur. This together with 3.5 gr, cut loose from the rough surface of the electrodes, was subjected to the same kind of chemical analysis as employed by Smits and Karssen. The method is mainly built upon a procedure described by Stock and Heller.[5] To separate the mercury from the bulk of the lead, the precipitation is brought into a quartz tube, which is heated to 800–900°C with a slow stream of hydrogen going through. The hydrogen takes the mercury along with it to a double U-tube where the latter is condensed, and by means of chemical methods one finally gets out the mercury in metallic form. It can also be converted into mercury iodide which forms easily distinguishable red crystals. An amount of 1/100 of a milligram of mercury can not be overlooked, and amounts of 1/1000 of a milligram of mercury as iodide can be rather easily detected under the microscope.

[5] Stock and Heller, Zeits. f. angew. Chem., 39, 466 (1926).

The result of the first run was an amount of mercury between 1/10 and 1/100 of a milligram. To make sure that there was no mercury in the electrodes, they were analyzed by melting them down and heating the lead in a stream of hydrogen, proceeding in the same way as with an analysis, but no mercury was found. Blind tests showed that no mercury came in through the chemicals used, and numerous tests with solutions of 1/10 to 1/100 mgr. of mercury, treated as in the analysis, showed, as far as could be judged, that the amounts could be recovered.

In the next experiment the above mentioned carbon bisulphide was used. To ascertain the purity of the lead, hydrogen was bubbled through it for 24 hours at 850°C and for 12 hours at 950°C. The purity was tested by heating it in the same vessel in a stream of hydrogen, and analyzing the distillate. No mercury could be detected. Then the actual run was started and a total time of 2 hours was attained. The amount of precipitated material amounted to 4.5 gr which, together with 3.5 gr from the electrodes was distilled and analyzed as before. The result was a very evident positive mercury reaction, but the amount was much less than before.

At the same time, a purification of the German lead from Kahlbaum was carried out by heating it for 20 hours at 950°C while hydrogen was bubbled through. Then the previously mentioned double U-tube was melted on, and an analysis performed, the difference from the previous analysis of lead for electrodes being that the hydrogen actually bubbled through the molten lead. This analysis gave mercury, although not very much. This seemed to show, that the procedure of leading hydrogen over the lead was an unreliable process of analysis, and the bubbling of hydrogen through the molten lead could not be relied upon for purification, when amounts of a hundred grams are involved. The electrodes used in the last experiment were then melted down, and an analysis performed by bubbling hydrogen through the liquid lead. This analysis, however, gave no mercury.

Previous experiments had shown that it was possible to get rid of the mercury by distilling it off in a high vacuum. Consequently half of the German lead in the container was driven over, and the residue was analyzed by leading hydrogen close over the surface of the lead. Due to experimental difficulties it was not possible to let the hydrogen bubble through the lead this time. This analysis gave no mercury. With this lead a run of 3.5 hours was performed, yielding about 11 gr of washed precipitate. This was analyzed in the usual way and gave only a slight mercury reaction.

The results of these runs seem to indicate that with a sufficient purification of the materials used, it is possible to reduce the amounts of mercury found, which again means that the mercury originates from electrodes, carbon bisulphide and dust coming in during the experiment. In a physical laboratory it is very hard to find places which are free from mercury. All dust must be suspected of containing it, and this necessitates an extreme cleanliness in handling all objects used.

Conclusions

As will be seen, the results of the experiments with the x-ray tube and also with the lead arc lamp are absolutely negative, although the extremely small possibility exists that Smits and Karssen chanced to establish some extraordinary experimental conditions whereby a transmutation is possible.

The experiments with the discharges in carbon bisulphide are not quite negative, but it is the authors opinion that it would be possible to get clean negative results with quite pure substances and under conditions where no accidental contamination was possible.

The author wants to express his gratitude to Dr. R. A. Millikan for helpful suggestions during the work.

In a letter from Smits[6] to "Nature" which appeared after this work had been finished, he states that the greater amount of mercury which he got in the experiments with discharges in carbon bisulphide, is due to contaminations. But he maintains that there is still a residual effect which can not be ascribed to that cause. In a later article by Smits and Frederikse[7] they describe a repetition of the experiment of Smits and Karssen with high potential discharges in carbon disulphide, in which their results were entirely negative. They think that the positive results previously obtained must be ascribed to impurities in the carbon disulphide used in the first experiments.

Norman Bridge Laboratory of Physics,
California Institute,
Pasadena, California,
September 25, 1928.

[6] Smits, Nature, **120**, 475 (1927).
[7] A. Smits and W. A. Frederikse, Zeits. f. Elektrochemie **34**, 350 (1928).

TWO ENERGY TYPES IN WAVE MOTION AND THEIR RELATION TO GROUP AND WAVE VELOCITY

By Lewi Tonks

Abstract

The energy of an element in a wave motion can be of two kinds: first, non-interactive like the energy of a set of independent pendulum bobs, and second, interactive like the potential energy of an element of a stretched string which is dependent only on the relative position of the neighboring elements. In the former case the group velocity is zero, and in the latter it equals the wave velocity. The slowing down of energy transmission in intermediate cases is discussed qualitatively and the ratio of group to wave velocity is calculated quantitatively in a number of cases on the assumption that the energy propagation is given not only by the product of energy density and group velocity, but also by the product of twice the interactive energy density and wave velocity. A general relation is suggested without proof for the connection between energy types and the ratio of group to wave velocity. The same ideas are applied to de Broglie's phase waves, the group velocity of which is the particle velocity.

IN A paper entitled "On Progressive Waves" Lord Rayleigh[1] gave a general proof of the fact that the group velocity of a wave train is the velocity of transfer of the wave energy. A recent theoretical investigation by Mr. Harold Mott-Smith, Jr. concerning an infinite wave train of electron oscillations in an ionized gas containing normally stationary electrons led to the result that such waves should have a constant frequency irrespective of wave-length.[2]

Now group velocity, u, in terms of wave velocity, v, and wave-length, λ, is given by the well-known expression

$$u = v - \lambda dv/d\lambda \tag{1}$$

When $f = v/\lambda$ is constant as in the present case, $u = 0$. Here is a strange case of a set of waves incapable of transmitting energy. Further analysis showed, however, that the electric field arising from a small and symmetrical local displacement of electrons does not extend beyond the edge of the disturbed region,[3] so that there are no forces which tend to spread the disturbance. A set of balls suspended each by a string from a ceiling to form pendulums of equal period which do not touch can, similarly, exhibit a wave motion which is incapable of propagation.

A comparison of these cases where the group velocity is zero with the vibration of a stretched string where the group and wave velocities are equal shows a striking difference in the nature of the energy of the vibration. In the latter case the whole potential energy arises from the mutual interaction of neighboring portions of the vibrating medium, in the former cases none.

[1] Rayleigh, Scientific Papers, Vol. 1, p. 322, or Proc. London Math. Soc. 9, 21 (1877).
[2] Langmuir, Proc. Nat. Acad. Sci. 14, 629 (1928).
[3] Tonks and Langmuir, Phys. Rev. (this issue) 33, 195 (1929).

This is, fundamentally, simply a restatement in another form of the confinement of the oscillatory field to the disturbed region, but its importance lies not in this extreme case so much as in cases intermediate between the two. In many cases the potential energy is partially of the one type, partially of the other. It is only the kind arising from interaction which has any propagative power. The speed of energy transfer is only sufficient to supply the new wave with twice the interactive energy, but before the new wave is complete additional non-interactive energy may have to be supplied. Accordingly, the completion of the new wave is delayed until this extra energy can be supplied via the interactive forces. It is this slowing down which constitutes the difference between wave and group velocity.

Quantitatively it has been found in the cases tried that the energy flow may be expressed by vE_i as well as by uE where E is the total average energy per unit length, and E_i is *twice* the total average interactive energy per unit length. It is immediately seen that waves on a stretched string behave this way, for $E_i=E$ (since one-half the total energy is interactive), whence $u=v$.

A slightly more complex case is essentially a combination of the stretched string and the pendulums. Suppose the stretched string to lie in the bottom of a smooth parabolic trough and let it be arranged so that when vibrating it always touches the trough throughout its length. If the string were divided into small sections, each section could oscillate independently like a pendulum. Let distance along the string be denoted by x, transverse displacement by y, tension and mass per cm of the string by T and m respectively. The equation of motion of an element of the string is then

$$T\partial^2 y/\partial x^2 - m\alpha y - m\partial^2 y/\partial t^2 = 0 \tag{2}$$

where α is a constant involving the gravitational constant and the curvature of the trough. Assuming the solution

$$y = y_0 \cos\left[2\pi(x-vt)/\lambda\right] \tag{3}$$

the wave velocity is found to be

$$v = (T/m + \lambda^2\alpha/4\pi^2)^{1/2} \tag{4}$$

and the group velocity is less, being

$$u = v - \alpha\lambda^2/4\pi^2 v = T/mv \tag{5}$$

The total energy per cm is

$$E = (1/2)m(\partial y/\partial t)^2_{max}$$

which, using (3), becomes

$$E = 2\pi^2 m v^2 y_0^2/\lambda^2 \tag{6}$$

Thus, the energy flow is

$$uE = 2\pi^2 v T y_0^2/\lambda^2 \tag{7}$$

The interactive energy of the string is its energy of deformation. For a length dx it is $(-T/2)y(\partial^2 y/\partial x^2)dx$. Substitution from Eq. (3) and integration over one wave-length gives the interactive energy per wave-length. Division of this by λ to find the average value, and then multiplication by 2 gives

$$E_i = 2\pi^2 T y_0^2/\lambda^2.$$

Comparison with Eq. (7) shows immediately that

$$uE = vE_i \tag{8}$$

If the string is laid along the vertex of a parabolic ridge the gravitational energy is negative so that the total energy is less than twice the interactive energy. In this case the group velocity is greater than the wave velocity, for $\alpha < 0$ for a ridge. The longer the wave-length the less the total energy, the slower the waves and the faster the group until a limiting wave-length is reached at which the tension is insufficient to keep the string on the vertex of the ridge.

The same idea slightly modified can be extended to deep and shallow gravity waves in a fluid. In these cases, the interactive energy is kinetic since the potential energy of an element, being gravitational, is independent of its neighbors, and non-interactive. In deep gravity waves each particle describes a circle. The horizontal component of the motion is effective in transmitting energy, the vertical component (except for viscosity) is not, hence only one-half the average kinetic energy is interactive. Thus twice the interactive kinetic energy is one-half the total energy, and the group velocity is half the wave velocity. In shallow waves, on the other hand, the vertical motion is negligible, all the kinetic energy is interactive and $u = v$.

Ripples are short waves on the surface of a liquid whose main potential energy is in the form of surface extension. Their group velocity exceeds their wave velocity, u being three-halves of v in the limit as the wave-length decreases. As in the deep gravity waves the particles describe circles, but unlike them the potential energy of the shortest waves, depending only on the relative positions of surface elements, is wholly interactive. Thus the interaction of the potential energy alone would be sufficient to propagate energy with full wave velocity, but in addition one-half of the kinetic energy is also interactive. The interactive energy, $E_i/2$, thus totals $(3/4)E$ with the result that

$$u = (3/2)v$$

by Eq. (8)

A generalization may be possible in the following form: Denoting the average interactive energies of various types in a unit length of wave motion by $I_1, I_2, \cdots, I_k$, and the average total energy per unit length by E, the relation between group and wave velocities is

$$u = 2v \sum I_n/E \tag{9}$$

This is, fundamentally, simply a restatement in another form of the confinement of the oscillatory field to the disturbed region, but its importance lies not in this extreme case so much as in cases intermediate between the two. In many cases the potential energy is partially of the one type, partially of the other. It is only the kind arising from interaction which has any propagative power. The speed of energy transfer is only sufficient to supply the new wave with twice the interactive energy, but before the new wave is complete additional non-interactive energy may have to be supplied. Accordingly, the completion of the new wave is delayed until this extra energy can be supplied via the interactive forces. It is this slowing down which constitutes the difference between wave and group velocity.

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Using I_p for the average interactive potential, I_k for the average interactive kinetic energy in the several examples cited, the values of I_p/E and I_k/E have been:

Type of Wave Motion	I_p/E	I_k/E
Electrons in ionized gas Independent pendulums	0	0
Stretched string	0.5	0
String in trough	<0.5	0
String on ridge	>0.5	0
Deep gravity waves	0	0.25
Shallow gravity waves	0	0.5
Ripples (short wave limit)	0.5	0.25

A possible connection with undulatory dynamics[4] immediately suggests itself. There the particle velocity is given by the group and not the wave (phase) velocity of the phase waves. When we examine the energy associated with the system it appears that only the kinetic energy, T, of the particle is interactive. Putting $I=T$, Eq. (9) becomes

$$u=(2T/E)v \tag{10}$$

This same relation is found by combining the expressions for group and wave velocity which are given by Schrödinger, namely

$$u=[2(E-V)/m]^{1/2}\,;\quad v=E/[2m(E-V)]^{1/2}$$

V being the potential energy of the particle.

The attempt to devise a general proof will undoubtedly lead to a rigorous definition of interactive energy and bring out the limitations of the concepts developed in the present paper. The proof will, it is thought, depend essentially on an enumeration of the forms of the terms in the differential equation of the motion, but boundary conditions (consider deep as against shallow gravity waves) will also be involved.

The present author does not desire to pursue this matter further and believes that publication in the present incompleteness is justified by an apparent general desire for a clearer grasp of the relation of group to wave velocity.

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[4] L. de Broglie, Ann. d. Physique **3**, 22 (1925) or E. Schrödinger, Phys. Rev. **28**, 1049 1926). Schrödinger uses u and v in just the opposite sense to that employed here.

THE SPECIFIC HEAT OF MOLYBDENUM FROM 250°C TO −40°C*

By D. Cooper and G. O. Langstroth

Abstract

By the use of a long covered tube in the calorimeter proper of an ordinary Richards adiabatic calorimeter, values for the heat capacities of metals from high temperatures may be obtained, even when the falling body is not protected from radiation losses by a metal jacket. The experimental procedure for such a determination is given. A calorimeter arrangement in which the metal was first partially cooled in the calorimeter and then allowed to come in contact with the water of the calorimeter proved unsuitable as is shown. The specific heats of molybdenum between the temperatures of −30°C and 300°C are given by the following equation with an accuracy of about one percent.

$$C_p = 0.0593 + 0.000013(T+40) - 0.0265/(T+40)^{1.08}$$

Stern's equation, which is linear agrees with the values given between 50°C and 300°C. Below 50°C the curve shows a decided bend.

A GLANCE through the literature reveals the fact that the data on the specific heat of molybdenum are far from satisfactory. Extreme values show a discrepancy of about 14 percent. This is admirably summarized in a paper by Van Voorhis[1] who points out that neither are the experimental values in agreement with one another, nor do they agree with the theoretical curves. A survey of the literature also shows that no adiabatic method for the determination of the mean specific heats has been used, and in view of the fact that this method offers considerable advantage from the point of view of experimental accuracy over similar methods using an ordinary calorimeter, a calorimeter was devised which, it is believed, gives the values of the specific heats of molybdenum with an experimental accuracy of about one percent.

Apparatus

The apparatus used was the ordinary type[2] of Richard's adiabatic calorimeter, the inner vessel of which, (now termed the calorimeter), was constructed to hold about 400 cc of water.

Two types of calorimeters were tried. The first allowed the hot molybdenum to come into contact with the water of the calorimeter; the second was so designed that throughout the duration of an experiment the metal remained dry. Both types are described here in order to give some idea of the nature of the errors introduced in this type of calorimeter measurement by the escape of very small amounts of steam.

* One of the authors wishes to express his thanks to the National Research Council of Canada, a bursary from which enabled this work to be carried out.

[1] Van Voorhis, Phys. Rev. **30**, 318 (1927).

[2] See Maass and Waldbauer, Jour. Am. Chem. Soc. **47**, 1 (1925).

The first calorimeter took the form of that shown in Fig. 1. It consisted of a copper vessel of about 400 cc capacity, to the bottom of which were soldered three spring clips *A* which supported a smaller copper vessel *B* fitted with a tightly fitting cover *C*. The molybdenum when allowed to drop into the calorimeter, struck the automatic trip of the cover, closed it tightly, and by the force of impact dislodged the vessel *B* so that it was forced down till it became totally immersed in the water of the calorimeter. At the commencement of a run the vessel *B* was dry. Experiments with the molybdenum at a temperature of 300°C and the calorimeter exposed so that the effect of the entrance of the molybdenum could be seen, disclosed the fact that the metal when allowed to drop into *B* first closed the cover, forced the vessel under water, and for an appreciable length of time remained dry. After the vessel had become immersed, there always escaped a few bubbles which were thought to consist only of displaced air. However results which will be given later point only to one fact, namely that with this type of apparatus there was some escape of steam, which although too slight to be noticed nevertheless had a very appreciable effect on the results. The authors wish to emphasize this fact because they feel that in some previous work of this nature several experimenters failed to take sufficient precautions to prevent steam effects when working with metals at high temperatures using analagous methods with different types of calorimeters.

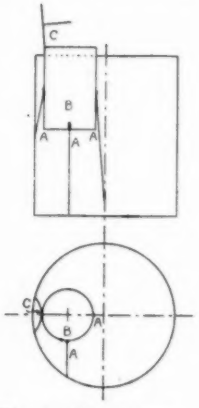

Fig. 1. First form of calorimeter.

The second calorimeter took the form of that shown in Fig. 2. It consisted of a long copper vessel in which was fastened a copper tube so arranged that its top extended above the surface of the water in the calorimeter. The copper tube could be centered under the reaction tube of the calorimeter bomb, and after the entrance of the molybdenum a cover fitted to the tube could be closed by means of a silk thread brought out through the thermocouple tube. This cover prevented heat losses by convection currents brought about by the entrance of the hot metal. The calorimeter and tube were of such length that in the authors' opinion they offered no opportunity for heat losses by convection or conduction along the length of the tube. With this apparatus it was found possible to repeat results within the limits of calculated experimental errors, and unless some unknown constant error was present these results are correct within the limits of experimental error (*q. v.*).

Fig. 2. Second form of calorimeter.

The molybdenum was heated to the desired temperature by means of an electric furnace of the resistance type, the design of which is shown in Fig. 3. The air space about the center tube in which the metal was

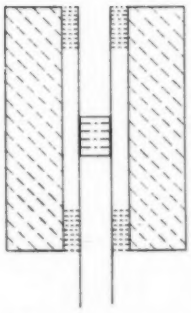

Fig. 3. Design of electric furnace.

suspended allowed equilization of temperature throughout the used part of the furnace tube. The temperature of the molybdenum was read by means of a high temperature mercury thermometer in tenths of degrees, standardized by means of a thermocouple in such a way that it was unnecessary to correct for the exposed length of stem.

The thermometer used in reading difference of temperature of the calorimeter was one that had been standardized by the Reichsanstalt and calibrated to the nearest thousandth of a degree. The auxilliary thermometers were also checked against standard thermometers supplied by the Reichsanstalt.

Experimental Method

The metal was suspended in the furnace tube by means of a fine copper wire and the furnace allowed to heat till it had reached the desired temperature. Meanwhile, the calorimeter was filled with water at such a temperature that the final temperature at the end of the run would be as close as possible to that desired. The whole was weighed, adjusted, and placed in the bomb, sealed, and the calorimeter-bath stirrers started. Readings were taken every five minutes till the temperature remained constant within the error of reading the Beckmann. This usually occupied about twenty minutes during which time the furnace was held at the desired temperature within two-tenths of one degree, making in all a period of approximately forty-five minutes heating at the desired temperature. The reaction tube was then opened, the furnace cut off, carried to the calorimeter, and the metal allowed to drop; the cover of the copper tube was closed immediately and the stirrers again started. No difference in the furnace temperature could be noted when it had again reached its stand. Attention was paid to the regulation of the outer bath so at no time during the transfer of heat did the outer bath differ from the inner by more than 0.08°C. Heat transfer at this temperature difference is negligible for short periods of time. After the large preliminary heat change the temperature of the outer bath could be held to that of the calorimeter to approximately 0.002°C. For periods under two hours heat transfer at this temperature difference is negligible. After the heat change had apparently ceased, readings of the Beckmann were again taken till they remained constant as before. The calorimeter and the outer bath could be adjusted to a temperature difference of 0.0008°C and introduced no appreciable error in the temperature difference. Subtraction of the two Beckmann readings gave the rise in temperature of the calorimeter.

Results

The heat capacities were calculated from the rise in temperature of the water in the calorimeter, the weight of water, the water equivalent of the calorimeter, and the weight of the molybdenum. In speaking of heat capacities we mean the heat given out by the metal in cooling from the high

temperature to the final temperature of the calorimeter. The values of the heat capacities per grm. were plotted against the high temperature, and a smooth curve was drawn to fit them as closely as possible. A subtraction of the values at any two points on the curve gives the quantity of heat given out by one gram of the molybdenum in cooling from one temperature to the other. Dividing by the temperature difference gives the mean specific heat between these temperatures. These values were plotted at the mean temperature. Specific heats were thus obtained as mean values for every one hundred degrees; for example the specific heat from 300°C to 200°C was plotted at 250°C; from 275°C to 175°C at 225°C and so on. This method gives the mean values of the specific heat at every 25 degrees.

This method of plotting is possible because of the very regular curvature of the heat capacity curve, which means that the specific heat curve is nearly, if not quite a straight line above 30°C.

Table I gives the data from which the heat capacity curve was drawn, and Table II the values of the specific heat as obtained from the heat capacity curve. The curves are shown in Fig. 4.

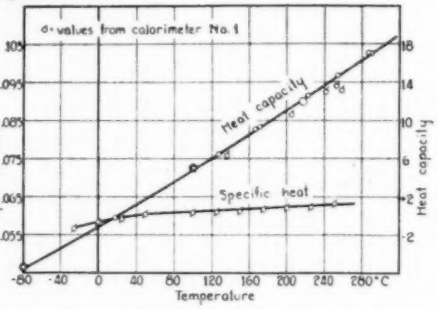

Fig. 4. Heat capacity and specific heat of molybdenum as a function of temperature.

TABLE I. *Data for heat capacity curve.*

Mo Temp.	Temp. Rise	Wt. water and cal.	Water Eq.	Heat Cap. per gm.
166.7	1.564	739.5	451.0	9.22
171.1	1.612	742.2	453.7	9.57
219.2	2.076	743.4	454.9	12.4
217.8	2.032	743.0	454.5	12.1
286.1	2.801	740.2	451.8	16.6
290.0	2.899	740.0	451.7	17.1
253.7	2.469	747.0	458.7	14.8
222.0	2.131	741.4	452.9	12.7
122.7	1.161	726.5	438.0	6.69
101.0	.919	722.7	434.2	5.26
−78.5	.724	807.6	571.5	5.30
−78.5	.726	805.5	569.4	5.30

TABLE II. *Specific heat of Mo at various temperatures.*

Temp.	Sp. heat	Temp.	Sp. heat	Temp.	Sp. heat
250	0.0632	125	0.0614	25	0.0597
225	.0625	100	.0612	0	.0589
200	.0624	75	.0613	−25	.0571
175	.0620	50	.0609	−40	.0564
150	.0616				

Since there are only three points below 20°C, and since there is evidently quite a bend in the curve below this temperature we do not claim a very high

accuracy for this part of the specific heat curve, but consider that it gives a fair idea of the shape of the curve. Above this temperature the curve is firmly established.

Experimental Errors

The errors of reading give a maximum error of 0.8 percent in the lowest heat capacity numbers, and one of 0.3 percent in the highest. In calculating the specific heat from two heat capacity values the error is increased to 1.4 percent which with an error of 1 percent in the temperature difference makes a total error of 2.4 percent in the value of the specific heat. Since the heat capacity values were averaged by drawing through them a smooth curve, the error in any single value is less than the maximum calculated error, which correspondingly lessens the error in the specific heat curve. In the same manner the specific heats were averaged by means of a smooth curve, the error in the single points thus being lessened. This reduces the error below 2.4 percent for a single point, and this method of average probably makes the actual error in any single point about 1 percent.

It will be noted that all points fall very closely on the heat capacity curve when the determinations were made with the calorimeter of the second type. No runs made with this calorimeter were discarded.

It will be recalled that mention of the unsatisfactory character of the results obtained with the first type of calorimeter has been made. It is interesting to note that without a single exception the values of the heat capacities calculated from data obtained with this calorimeter fell on the low side of the heat capacity curve. That the calorimetric measurement was not at fault was shown by making two determinations from the carbon-dioxide-ether point. These results are given above, and show that when the conditions were such that loss of heat by steam was impossible, the first type of calorimeter was satisfactory. Hence we conclude that in nearly, if not in all, of the determinations made with the first type of apparatus there was a loss of steam sufficient in amount to affect the results materially.

The numerical data for this preliminary work are not interesting, and since the whole series was discarded the results are omitted with the exception of a few points which will be found in Fig. 4 illustrating the curve from which the results were obtained.

Discussion of Results

The curve obtained is of the same form as Debye's theoretical curve,[1] and lies quite close to it; the greatest discrepancy is about 3.2 percent. It also follows the General Electric curve to some extent.[1] All experimental values except those of Stern[3] fall much higher. Those of Defacqz, Guichard, and Stücker as given by the Landolt and Börnstein Tables differ by about 14 percent from the theoretical curves. The three values just cited were obtained with molybdenum containing about 0.22 percent impurities.

[3] Stern, Phys Rev. **32**, 298 (1928).

White[4] has found that a small percentage of iridium raises the specific heat of platinum by a considerable amount. Any substance which is not mechanically held in the molybdenum would probably cause an increase in the specific heat, and this fact may account for the higher values obtained by the earlier experimenters.

TABLE III. *Comparison of the present results with those of Stern*

Temp. °C	Specific heat (Stern)	Specific heat (Authors)
0	0.05973	0.0589
50	.06054	.0609
100	.06134	.0612
200	.06296	.0624
250	.06377	.0632

Reference to Table III in which column 2 gives values calculated from the equation of Stern, and column 3 those obtained experimentally by the authors, shows that the results are in agreement for all values of temperature higher than 50°C.

From two values of specific heats, one the mean from 0°C to 100°C and the other the mean from 0°C to 444.5°C, Stern derives a linear equation for C_p. The equation obtained by the authors was taken from a curve which was fixed by 13 points (from $-40°$ to 250°C), calculated from a heat capacity curve which was fixed by 13 points (from $-78.5°$ to 300°C). Hence the curve obtained is quite definitely not a straight line but approaches very near to it at temperatures above 50°C. The equation takes the following form, and holds for all temperatures between $-30°$ and 300°C (T is in degrees Centigrade).

$$C_p = 0.0593 + 0.000013(T+40) - 0.0265/(T+40)^{1.06}$$

The sample of molybdenum used was obtained from the General Electric Company. It was not analysed in this laboratory.

DALHOUSIE UNIVERSITY,
HALIFAX N. S., CANADA.
September 24, 1928.

[4] White, Phys. Rev. 17, 438 (1918).

THERMAL CONDUCTIVITY OF LEAD AND OF SINGLE AND POLY CRYSTAL ZINC

By C. C. Bidwell and E. J. Lewis

Abstract

The thermal conductivities of lead and of single and poly crystal zinc over the temperature range −250°C to +100°C determined by a method previously described by Bidwell are reported upon. The thermal conductivity increases for these metals as the temperature is lowered but shows no extraordinary increase at extreme low temperatures as was found for lithium. The single crystal zinc shows about 18 percent better thermal conductivity than the poly crystal sample. A zinc sample cast in open air showed about 7 percent poorer conductivity than a sample prepared in vacuo. The data are in agreement with the law $k/aC=K/T+K'$.

AN adaptation of the Forbes bar method yielding precise measurements of thermal conductivity of metals was described in a recent paper[1] and values for sodium and lithium over a considerable temperature range were shown. The present report presents observations on thermal conductivity of lead and of single and poly crystal zinc over the temperature range −250°C to +100°C.

The theory of the method is given in the paper mentioned and the experimental details there fully described. The rods were of the same dimensions as those used in the work on the alkali metals and were mounted in the same glass tubes. This made possible the use of the cooling data on copper, lead and silver obtained in the earlier work to check the correctness of the heat loss curves on the zinc rods. Thermal conductivity was computed from the equation,

$$kA\left[(dT/dx)_1-(dT/dx)_2\right]=\frac{Be^d}{b}\left[e^{bx_2}-e^{bx_1}\right]+B(T_0-T_s)\left[x_2-x_1\right] \qquad (1)$$

The derivation of this has been shown.[1] The constants are obtained from the auxiliary equations

$$(1/L)MsdT/dt=BT-BT_s \qquad (2)$$

$$dT/dx=bT-bT_0 \qquad (3)$$

$$\log_e(T-T_0)=bx+d \qquad (4)$$

The rods in this work were used bare, whereas in the previous work the alkali metal rods were wrapped in a single layer of paper and kept under nujol while not in use in order to prevent oxidation. For uniformity of surface all rods were wrapped in oil soaked paper which was tightly wound on and tied with thread. Thus all rods of whatever material presented the same surface and yielded the same heat loss rate per cm at the same temperature. In the

[1] Bidwell, Phys. Rev. **28**, 584–597 (1926).

present work it was thought best to discard the paper covering. Therefore, cooling data on bare lead and zinc rods of the same dimensions were obtained to supplement the previous cooling data on the wrapped specimens. Exactly the same heat loss curves were found for copper, silver, lead and zinc at the lower temperatures, notwithstanding the fact that the copper and silver were wrapped and the lead and zinc bare. At the ice and steam temperatures the wrapped rods showed a progressively greater heat loss rate than the bare rods indicating that differences in radiating power become a factor at the higher temperatures. The data for the three zinc rods are shown in Fig. 1 and for the lead specimen in Fig. 2.[2]

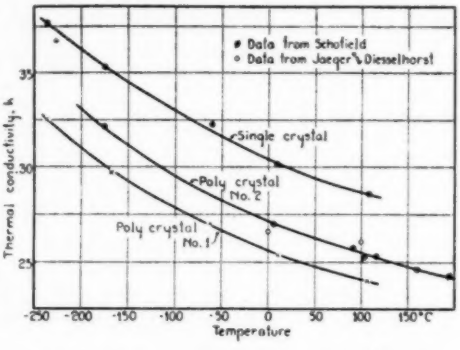

Fig. 1. Thermal conductivity of zinc.

For zinc rod No. 1 the metal was melted in the open air and poured into a graphite mold. Rod No. 2 was cast in vacuo to avoid oxide contamination. The thermal conductivity of rod No. 2 was found to be about 7 percent better, thus indicating the effect either of slight oxide contamination or possibly of variation in crystal size. The increase in conductivity as temperature is lowered is similar for all rods. The thermal conductivity of the single crystal zinc is about 18 percent better at room temperature than the poly crystal rod, No. 2. There is no disproportionate increase in k at extreme low temperatures as was found for lithium[1] and as had been reported for copper and gold.[3] Some thermal conductivity values for zinc at upper temperature ranges have been reported by Schofield[4] and by Jaeger and Diesselhorst.[5] These data are also shown in Fig. 1. The very good agreement

[2] The zinc used in this work was obtained from the Bureau of Standards and the analysis was given as 99.993 zinc with 0.005 percent Fe, 0.0018 percent Cd. The lead was also obtained from the Bureau of Standards, as very high purity lead. Its analysis was not available. The single crystal zinc rod was prepared by following directions given by Bridgman, Am. Acad. Proc. **60**, 305 (1925)). It was melted in an exhausted glass tube containing a constriction at the lower end and lowered from the furnace at the rate of 1 cm per hour. The glass was afterwards broken away with pliers. The rod presented the velvety appearance characteristic of single crystal structure and showed four brilliant flashes 90 degs. apart when illuminated by a single distant light and rotated. The basal planes were further located as parallel to the axis of the rod by making saw cuts at each end and splitting away sections by wedging a tool into the cut, the ruptures occuring along the basal or cleavage planes. According to Bridgman the preferred manner of growth is with the basal plane parallel to the axis of the cylinder. "The density of the atoms is greatest in the basal plane so that they pile themselves into the crystal more rapidly in this direction, the forces being greatest because of proximity." The increased thermal conductivity in the direction along the axis thus seems to be related to the greater density of atoms in this direction.

[3] Grüneisen and Goens, Zeits f. Physik **44**, 615 (1927).

[4] Schofield, Proc. Roy. Soc. Lond. **A107**, 227 (1925).

[5] Jaeger and Diesselhorst, Wiss Abh. Phys. Tech. Reich. 3 (1900).

of these points with the present data (on rod No. 2) affords additional confidence in the method here described. The course of the lead curve shows considerable variation from previously reported data by Meisner and by Schott, as given in the Landolt-Börnstein tables, but is in agreement with data from these tables by Macchia. A. Eucken[6] finds that for pure antimony and bismuth the thermal conductivity decreases strongly with decreased in size. The same thing is here shown for zinc, the single crystal rod being much the better conductor.

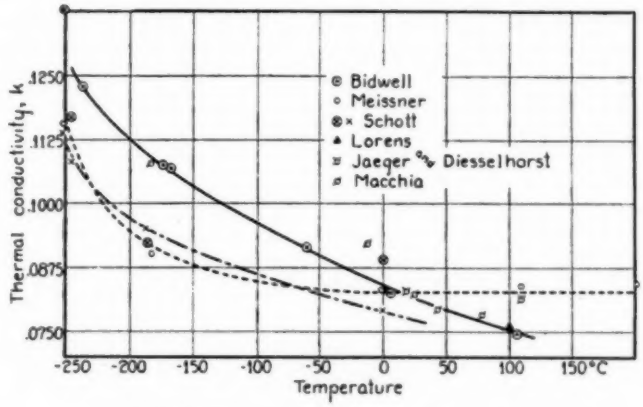

Fig. 2. Thermal conductivity of lead.

The present data on zinc and lead are in agreement with the law $k/aC=K/T+K'$, where k is the thermal conductivity; aC, the atomic heat; T, the absolute temperature; and K and K' constants.[7] The lines shown in the paper mentioned[7] include the data on zinc and lead herein reported. The fact that the data of Meissner and Schott on lead do not agree with this law while our newer data and the data of Macchia do, argues for the correctness of our data.

LEHIGH UNIVERSITY,
CORNELL UNIVERSITY,
March 30, 1928.*

[6] Eucken, Zeits. f. Tech. Phys. **6**, 689 (1925).
[7] Bidwell, Phys. Rev. **32**, 311 (1928).
* Received August 12, 1928. Ed.

THE INFLUENCE OF SURFACE CONDITIONS ON THE FRICTION OF METALS

By R. B. Dow

Abstract

The present investigation, by an improved tilt method, attempts accurately to determine the static coefficient of friction for metallic surfaces under varying surface conditions in different media. The presence and nature of oxide films materially affect the rise of the friction curve; a thin film acting as an abrasive causes the curve to rise, the rate depending on the normal force, until a layer of increased stability is reached. In terms of surface flow this indicates the formation of a vitreous layer. Thick films of certain oxides act as lubricants of great stability. Area of rubbing, shape of surfaces, and dry gases have no influence on μ; moist inert gases show a capillary effect, moist active gases destroy the surfaces. μ is found to be a linear function of the number of slips of one surface over another.

Introduction

THE difficulty of adequately controlling surface conditions involved in friction measurements has been such that no precise interpretation can be made of the phenomena through the values obtained for the coefficient by the usual methods. Methods of cleaning have not been satisfactory, the areas of the surfaces have been too great to give the value of μ at a point, and the effect of atmospheric conditions have been so neglected that, for metal surfaces, values of μ have greatly varied. The conditions of the surfaces just as motion is impending are most easily studied by knowing the static coefficient at a certain point. In this paper, I shall discuss the influence of surface conditions on the friction of some metals and give characteristic values for surfaces under various conditions.

Method of Cleaning Surfaces

(1) Any roughness of surface was removed with no 0.0004 flint paper. (2) The surfaces were carefully polished with Crocus cloth and oil. (3) Fine machine oil was used to clean away the metal dust. (4) The surfaces were washed in CCl_4 to free from oil. (5) The surfaces were boiled in distilled water for 15 min. (6) The surfaces were then washed under the tap and allowed to dry in air. Whatman filter paper was used to wipe and handle the rods. The surfaces were polished to such an extent by the above procedure before each test, that under the microscope fine longitudinal lines were visible but no tears in the surfaces were noticeable. A low power microscope was used. This method gave consistent average results.

Apparatus

The tilt method of determining μ devised by P. E. Shaw[1] was used with an automatic control arrangement and modified for work in vacuo. Fig. 1 shows

[1] P. E. Shaw, Jour. of Sci. Instruments **4**, 222 (1927).

the essentials of the apparatus that was used for the tests in air. A short length of the rod to be tested is clamped across the table of the apparatus. A longer rod of the same material, supported equally by a fine copper wire bifilar at one end and by the fixed rod at the other, slides transversely across the fixed rod when the table is tilted beyond the critical angle by means of weights, the cords of which act on the table arm through pulleys. The sliding rod and one of the end contacts complete a low voltage relay circuit which operates an electromagnetic stopping device. This device serves to stop the tilt by locking the cord of one of the weight pans when the sliding rod breaks the end contact. One weight pan submerged in a vessel of water controls the rate of tilt by opposing the action of the other pan of weights. The system operates smoothly and at a low rate of constant angular speed by simply adding or taking away water from the vessel. An optical lever on the axis of rotation determines the critical angle ϕ. One slide is considered as the result of two tilts of the apparatus, one clockwise and the other counter clockwise. For the work in vacuo, the whole apparatus was enclosed in a brass cylinder with plate-glass ends. A rack and pinion carrying a cleaning strip of Crocus cloth and filter paper served to clean the rods in vacuo at any desired stage of rubbing. Vacua of 0.1 mm were obtained and worked with conveniently. The sensitivity of the apparatus is given in terms of angular speed increase, per increase of pan load. An increase of 10 g in weight increased the angular speed by 1.5° per second.

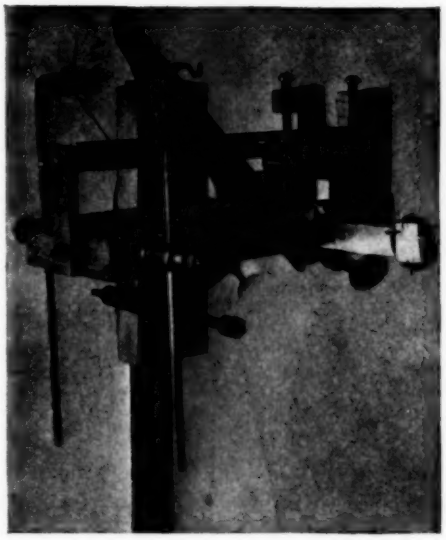

Fig. 1. Apparatus.

By this method, the angle of friction, ϕ, is clearly a function of the number of slips. The procedure was to study the stability of surface conditions by repeating the measurement of ϕ under different conditions. μ, a function of ϕ, was found by means of the tangent relation.

Results

The results in air indicated that the degree of oxidation of the surfaces determines the rise of the friction curve. A thin layer of oxide on brass acted as an abrasive, the nature of the film determining its abrasive character. The rate of rise of the curve depended on the normal force as shown in Fig. 2. The coefficient of friction in this case therefore depended on the normal force.

If the experiment was made a considerable time after polishing, μ was found to be constant, which was taken to mean that the oxide coating on the

surfaces of the metal was heavy and the rubbing layers of the oxide film were in a stable condition. No abrasive action appeared in this case and the low value of μ suggests that the heavy film acted as a lubricant to protect the metal surfaces. The constancy of μ for thick films is illustrated in Fig. 3, curve *b*. The data for this graph were taken in vacuo at pressures of about 0.1 mm. Curve *a* of the same figure shows that a like condition of stability was obtained but under different conditions. The curve shows the invariability of μ with change of normal force when two hard vitreous layers are rubbed together. The nature and formation of such layers will later be considered, but

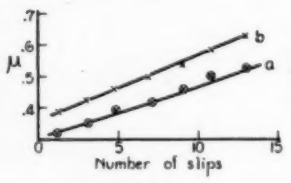

FIG. 2.

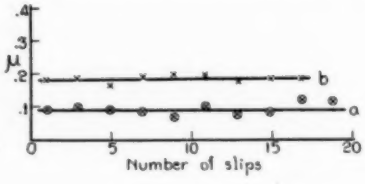

FIG. 3.

Fig. 2. Curves for brass; *a*, normal force is 64 g; *b*, normal force is 83 g; pressure, 0.1 mm.

Fig. 3. Curves for brass; *b*, thick oxide layer; *a*, independent of normal force; 29 g−40 g; pressure, 1.0 mm.

the same invariability of μ with normal force was found when thick films of oxide were rubbed together. The rather large deviation of the points about the mean is explained in part by the fact that for each change of normal force, air was admitted and the rubbing surfaces separated. But in the experiment, the normal force was not increased steadily but was varied from a high value to a low one and vice versa; an increase in load caused both a decline and rise of the curve which was due to slightly different surfaces in contact.

For aluminium oxide, the lubricating property of thick films was found to be absent and this is probably due to the extremely hard oxide which tore up the metal surfaces. The change in normal force was accomplished by filling a brass tube with substances of different densities to get the desired weight and then closing the ends with brass plugs.

The best controlled experiments were done in vacua with the air exhausted to varying degrees. The data obtained were similar to those found in air. Values obtained in vacuo were generally lower than those obtained in air but this was due to initial cleaning after evacuation. Some of the oxide was cleaned away and conditions were such that the remaining film did not grow. A change in vacuum did not appreciably influence the results because there was little growth in the oxide layer, and the great pressure at the point of contact of the curved surfaces was sufficient to squeeze out the air film.

Typical curves for brass and copper in vacuo are given in Fig. 4, curves *a* and *b*, respectively. The final constant ordinates of the curves show that the rods had attained a constant surface condition. This condition suggests a hard surface formation, a vitreous layer of increased stability formed as the result of earlier surface disturbances. This same sort of surface was produced

by polishing rods of brass and copper with Schmirgel and then wiping with filter paper. A source of bright light was so directed on the surfaces that diffraction patterns or lack of them were visible when viewed through a microscope. After the traces of dust had been carefully wiped away, it was found that a regular sort of lattice pattern was visible.

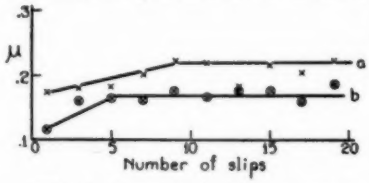

Fig. 4. Curve *a* for brass; curve *b* for copper; pressure, 1.0 mm.

Now if the molecules were displaced from their positions by the mechanical disturbance caused by polishing and a sort of flow resulted in the formation of a non-crystalline or vitreous state, high temperatures should aid the molecules in recovering from the strain and ensure their return to the crystalline state. To see if heating did have this effect, the polished surfaces were heated in two different ways. In the first case, the rods were boiled in distilled water for 30 minutes and were then allowed to cool in the water. After the rods were thoroughly dry, examination failed to reveal any sort of diffraction pattern. The effect approached that seen when the rods were in the crystalline condition. The second method was to hold the rods in the oxidizing flame of a Bunsen burner for about 3 minutes and then observe the optical effect immediately afterward. The possible formation of oxide did not effect the results in this case. Similarly, it was observed that heat released the strain and the molecular rearrangement took place when the elastic constraint was lessened. When rods polished in a similar manner were tested, it was found, as discussed above in the case of thick films of oxide, that μ did not vary with change in normal force.

Thick films of oxide and vitrified surfaces both exhibited stable conditions, as observed by the constancy of μ, for as many as 50 slips although they are of totally different nature. Thick films of oxide are produced by the natural growth of such spicular, granular substances under certain atmospheric conditions. Vitreous solids are produced as the result of a sort of crystalline flow that solidifies and leaves the molecules in a new arrangement which constitutes a hard surface. A much greater force is required to disturb a completely vitrified surface as compared with a crystalline one. Slipping of vitreous layers is accomplished without any appreciable surface deformation; tears in such surfaces caused by the presence of hard foreign particles, or the separation of welded areas are of greater importance in the resultant friction than the consideration of a flow that accompanies crystal slip.

Jeffrey[2] has recently shown that the surfaces of easiest slip for a vitreous solid are curved instead of plane. This offers a possible explanation why individual determinations of μ in the vitreous state fluctuate by an amount greater than the probable experimental error. With moisture in the testing chamber, the variation can be explained by instantaneous oxidation and the subsequent rubbing away of the oxide. The mean value, in this case, may be considered as the average value approached by several, separate, minor

[2] Jeffrey, Proc. Camb. Phil. Soc. **24**, 23 (1928).

curves which result from the rubbing of oxide particles between the vitreous surfaces; in each case, the constant condition was found after all the oxide had been rubbed away. The linear mean value taken as a constant shows the probable value that would be obtained if ideal rubbing conditions were obtained.

The possibility of gas films adhering to the surfaces of the metals was considered remote as the surfaces were mechanically disturbed by the wearing away action that accompanied each slip.

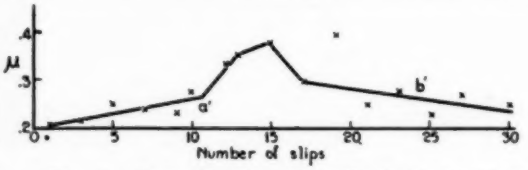

Fig. 5. Curve for zinc; a', moist O_2 let in· b', 20 hours later: pressure, 0.1 mm.

Fig. 5 shows the effect of a moist inert gas on the friction of zinc surfaces. Moist inert gases influenced μ only through capillarity. Dry inert gases, such as oxygen and hydrogen, did not effect μ. This corroborated the experiments of Charron.[3]

Fig. 6, curves a and b show the action of nitric acid and ozone, respectively, on different surfaces. Nitric acid destroyed the surface layer and left a spongy textured surface that rapidly gave away with each succeeding slip; μ decreased until a new metal surface was exposed. The curve for ozone shows the great oxidizing effect on the surfaces of zinc rods. The increasing steepness of the curve indicated the more rapid growth of the surface film of oxide.

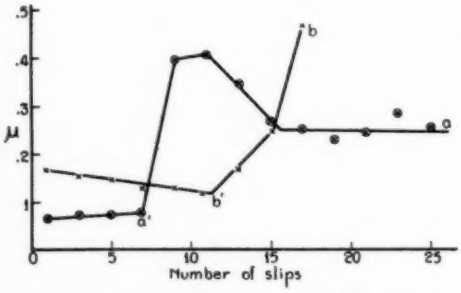

Fig. 6. Curve a for Cu; a', HNO_3 let in. Curve b for Zn; b', O_3 let in, pressure, 0.1 mm

Conclusion

The results suggest the following interpretation. Thick films of oxide, particularly soft oxides on hard metal surfaces, act as lubricants, the surface molecules re-orienting freely, yet the film being so thick that its stability is not effected by relatively slight changes in surface conditions, so that μ remains constant. Thin films break readily and the crystal structure of the metal is sheared with each rub. The mechanism of crystal slip is not completely known. The idea of a surface flow, such as the Beilby flow, that resolidifies into a vitreous layer after each slip seems useful in explaining the increased molecular stability that results from each slip until a final constant condition is reached. From the figures, it is evident that μ is a linear function of the number of slides. Analytically, this means that dy/dx is a constant. If we call y, the formation of vitreous material with each slip x, the rate of formation of vitreous material is constant with each slip until the resulting laminated structure, which is composed of alternate layers of crystalline

[3] Charron, Comptes Rendus **146**, 1013 (1908).

material sandwiched between layers of vitreous material, cleaves and two vitreous layers slip over each other, y then remains constant while x increases. This interpretation agrees with the results that should be obtained according to the Beilby idea, and the experimental results seem to justify the reality of such a flow. From this viewpoint, the nature of the flow is not the same as that of a viscous liquid, for in the present case there is a sharp transition point when the rise of μ suddenly stops and remains constant, independent of the number of following rubs. No attempt is made to estimate the thickness of a vitreous layer that results from a single slide. It must necessarily be very thin. The formation of each vitreous layer can be considered apart from the one next to it for the time of surface flow at a point is much less than the time required for one slide. Friction curves have usually been represented by a curved line, dy/dx changing until the curve asymptotically approached a constant value. This does not seem to be the case according to the above interpretation.

On the other hand, when the surfaces are covered with a heavy oxide layer, the mechanism is essentially that of one particle sliding over another, the metal surfaces being cushioned by the layers of oxide whose internal resistance to separation is less than the adhesion between the oxide and metal. If surface flow occurs, it should be governed by the kinetic theory. It should exhibit the properties of surface tension which should decrease with rise in temperature. Such a picture explains the decrease of μ found by Jacob[4] up to 200°C. The increase of μ with increase of temperature above 200°C would indicate the rubbing of vitreous layers together.

This work was done by me while a graduate student at Clark University and it is a pleasure to acknowledge the help and inspiration of Dr. R. H. Goddard who made this work possible. I am also very grateful to Professor P. W. Bridgman for advice regarding the preparation of the manuscript.

WORCESTER POLYTECHNIC INSTITUTE
October, 1928.

[4] Jacob, Ann. d. Physik **38**, 126 (1912).

NOTE ON THE TUBE-CORRECTION IN MEASUREMENTS OF THE VELOCITY OF SOUND IN GASES

By R. E. Cornish and E. D. Eastman

SINCE the preparation of our paper on this subject, appearing in the preceding issue, an article by Shilling and Partington (Phil. Mag. **6**, 920, (1928)) has appeared in which reply is made to our earlier criticism of their tube-corrections and of the specific heats obtained by them at high temperatures.

Concerning the tube-correction itself, we note the following points in their work. The error in the velocity of sound assumed for air at 0° is unknown, but may be of the order of 0.2 m/sec. (It differs by this amount, for example, from the recent careful determinations of Grüneisen and Merkel, Ref. 7.) This alone is enough to account for an error of 75 percent in the constant for their tube *D*, and 15 percent for tube *C*. Their results for tube *D* therefore confirms, within the limit of error, the Helmholtz-Kirchhoff equation. The deviation found in tube *C* may be real, and if so is easily accounted for by the roughness of the surface. It appears to us obvious that the equation cannot hold for porous or rough-surfaced tubes, since the ratio of surface to volume of the tube must determine the magnitude of the correction, and this is assumed in the equation to depend only upon the diameter of the tube. We should class such tubes with those containing dust. The discrepancy with tube *B* appears far outside the necessary error-limit and cannot, we believe, be accounted for by the relatively low thermal conductivity of silica. The magnitude of the correction should *decrease* with the conductivity. Moreover, in our opinion, even with this material the conductivity and heat capacity are sufficiently greater than those of air to be regarded as infinite, especially since only about 25 percent of the correction is due to thermal effects. This opinion is supported by the experiments cited previously of Dixon, Campbell and Parker, which offer a more severe test of the effect of the material of the tube than those of Shilling and Partington. We emphasize again that if such an effect is ever established the method of "calibration" is at once invalidated for the material in question. We believe, however, that it is not established in the case of silica. The close agreement of the corrected velocities in the three tubes, especially at the high temperatures where the corrections are quite large, we are unable to reconcile with these views. We are forced, therefore, to the belief that compensating errors, either systematic or accidental, are responsible.

We believe the values of the specific heats of gases at high temperatures presented by Shilling and Partington to be less accurate than is claimed by them. The errors by which they may have been affected, as it seems to us, are, beside the possibly inaccurate tube-corrections discussed above, imperfect temperature measurement and control and errors in determination

of frequency. The question of temperature is discussed in another paper (to appear as a Technical Paper of the Bureau of Mines). It remains only to explain our position relating to frequency. The first paper by Shilling and Partington referred only to the calibration by a "standard wave-meter," which obviously might be much in error. In a later paper, it was stated that their oscillator had been calibrated by the National Physical Laboratory. As the frequency of such an oscillator is likely to be changed in transportation, the published table of calibration is not necessarily convincing. In the most recent communication a steel bar standard is described, though the method by which its frequency was determined at the standardizing laboratory is still unknown to us. The values of the velocity in air obtained in the early measurements using the standard wave-meter are, however, essentially identical with those from the more refined methods most recently described, although the frequency assumed in the calculations appears to have been appreciably different. This fact no doubt indicates that the original wave-meter was more accurate than we had supposed probable.

Finally we should state that the sources of error mentioned by Shilling and Partington as affecting our measurements with hydrogen were adequately controlled.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CALIFORNIA,
December 28, 1928.

BOOK REVIEWS

Modern Physics. H. A. WILSON. Pp. 381, 72 figs. Blackie and Son Limited, London and Glasgow, 1928. 30 s.

In this book Professor Wilson has admirably succeeded in giving a concise but intelligible account of those things with which all serious students of physics should be familiar. At best the graduate student in physics today finds the task of orienting himself in the literature of the subject an arduous one. This little book of Professor Wilson's is adapted to give the student the necessary background of fact and theory to enable him to begin an intelligent and appreciative reading of the current literature. Considering the size of the book the number of subjects treated is amazing. There are chapters on electron theory, magnetism, thermionics, photoelectricity, quantum theory, critical potentials, x-rays and γ-rays, optical spectra, cathode rays, β-rays and α-rays, positive rays, radioactivity, constitution of atoms, gaseous ions, motion of electrons in gases, conductivity of flames, positive column and negative glow, atmospheric electricity, special relativity, general relativity and gravitation, together with a final chapter of mathematical notes. To say nothing of a list of about 130 excellent problems at the back of the book, propounded in the best Cambridge style.

It is, of course, unavoidable, that, in compressing so much in 365 pages, many subjects are inadequately treated. For example, in the chapter dealing with the motion of electrons in gases, no mention is made of recent determinations of mean free path, of ionization efficiencies and the like. The sole reference is to Townsend's Electricity in Gases. Unfortunately, the author has made no attempt to include references to the original literature but has contented himself with references to standard treatises or bulletins dealing with the special topics.

JOHN T. TATE

Bibliography of Crystal Structure. JARED KIRTLAND MORSE. Pp. xx+164, 8 figs. University of Chicago Press, 1928. Price unbound, $3.00.

The title of this monograph errs by understatement. The introduction (pp. vii–xviii) describes the present facilities for crystal structure studies in the Ryerson Physical Laboratory, proposes the extension of these facilities, and recounts what has already been accomplished with them. Part I of the text (pp. 1–33) reinforces the introduction by reprinting six contributions from the Crystal Structure Laboratory (five by J. K. Morse and one by F. P. Goeder), all of which appeared in the Proceedings of the National Academy of Sciences in 1927 and 1928. These portions may best be considered together. The introduction shows signs of haste in preparation (*e.g.* Siemens for Seeman, Jessie for Jesse) and contains some awkward phrases (*e.g.* "method of Laue spots") and involved sentences (*e.g.* middle of p. xiv.). It contains some useful notes on the construction of filament transformers. In the reprints about a dozen mistakes in calculated coordinates and in references remain uncorrected and a few new ones appear. The reviewer feels also that a preference for cubic atoms goes too far when, as in the case of the structure proposed for crystals of graphite, the consecutive layers of atoms in basal planes have more than enough room between them for inserting complete layers of the same sort. The author rather surprisingly fails to point out that his benzene "ring" has holohedral cubic symmetry.

The bibliography itself (Pt. II, pp. 37–164) represents a large amount of work and should prove useful to any serious student of the subject. There are just over 1800 entries and though a few refer to papers only remotely connected with crystal or molecular structure, or are to abstracts and other secondary publications, most are properly included. The reviewer notes the omission of about 400 titles well within the scope of the list presented. The usefulness of the bibliography is reduced by the presence of many trivial errors. A rough check of about 1400 entries disclosed more than 250 in which the content or form was defective, the most prevalent mistake being in the page numbers. The reviewer has found in work of this kind

that writing final page numbers in full cuts down mistakes. There are about fifty errors in the spelling of author's names. A few of these are due to an occasional attempt to standardize the spelling of Russian names. The use of "de," "van" and "von" in fixing alphabetic order is also unusual and confusing. Aside from displacements due to the causes just mentioned there are about 25 errors in alphabetical arrangement and the entries under any one author for any one year are not put down in any definite order. About 15 entries are in the wrong year. The translation into English of titles in foreign languages is of doubtful expediency even when well done. Here the translations are often inexact and sometimes completely misleading. Titles in English are sometimes cut down too much. A few cross-references are given but most are to papers that are prominently referred to in the principal paper, and all could be omitted without sensible loss.

The paper and printing are good, the use of paper back lets the book lie open easily but has no other advantage. The price is rather high.

L. W. McKeehan

Lehrbuch der Kristallphysik (mit Ausschluss der Kristalloptik). Woldemar Voigt. Pp. xxvi+978, 213 figs., 1 table. B. G. Teubner, Leipzig and Berlin, 1928. Price bound 41.00 RM.

This is a reprint of the first and only edition of this standard work, that of 1910, long out of print but still indispensible to the student of crystal behavior. A brief note of introduction by von Laue points out that the demand for copies has risen sharply since the application of piezoelectricity in high frequency control. This is only one of the reasons for reawakened interest in the properties of crystals. The multitude of references to this work in the intervening literature of the subject are, of course, as accessible with the new as with the old printing since the pagination is the same in both. A few typographical errors have been corrected in accordance with the copy used by Voigt himself.

It might be thought by the unwary that anything written about crystals more than eighteen years ago must now be obsolete. On the contrary we must regard it as fortunate that the author completed his compendium just before the discovery of the diffraction of x-rays by crystals opened new avenues of attack upon the problems of crystal structure. He produced a classic which can only be surpassed, if ever, when the facts now being observed have been assimilated into a theory of the crystalline state in terms of atomic interplay. For the long meanwhile "Voigt" will be the convenient starting point for the description and explanation of macroscopic phenomena.

To the two appendices originally included has been added a third (not noted in the table of contents). This is a 14-page reprint of a paper published in 1915, wherein Voigt discusses some secondary effects due to twisting (or bending) in piezoelectric excitation.

The paper is less highly finished than that of the 1910 issue, and takes the ink rather better so that the page is appreciably blacker. In consequence the finer detail of the figures suffers a little but the text is easier to read and the general effect is more pleasing. The new binding is perhaps a little less substantial than the old. The price is low for so large a volume.

L. W. McKeehan

Heat and Thermodynamics. J. K. Roberts. Pp. 454. Blackie and Sons, 1928. Price 30 s.

The first sentence of the preface states that "this book has been written at the request of the publishers for the use of students taking a University Honours Course in Physics." The reader in this country will not, however, be interested in the success of the book in its primary purpose, however great that success may be, and this review will be written from the point of view of the American reader.

The book contains an enormous amount of material, over half the pages being in fine print. Besides the topics usually dealt with in books of this class, including applications to physical chemistry and engineering, there are chapters on the kinetic theory of gases and on radiation. The most important modern developments are taken care of in chapters on Nernst's Heat Theorem, on Debye's theory of specific heat, and on the equation of state of solids. The emphasis of the book is perhaps on the experimental rather than the theoretical side, and it is

natural that the English work with which the author, who was formerly assistant in the Heat Division of the National Physical Laboratory, is most immediately familiar, should be described in some detail. The reader will be glad to have the accounts of the admirable work of Callendar and of Griffiths. The reader will miss, however, certain other topics; for example, the classical results of Amagat on the properties of liquids and gases are not mentioned. The second law of thermodynamics is not taken up until the second half of the book; although the material of the first half has been skillfully arranged so that this is not necessary, it would seem that the student could have better understood some of the topics treated in the first half, such as the chemical constants for example, if he had had the second law at his command.

For general use the book seems to suffer from the limitations imposed by the special purpose for which it was written. It gives too much the atmosphere of hurry, there is too little differentiation of the important from the incidental, the historical point of view is not introduced so that the student is not brought to see the development of the subject from a few simple fundamental concepts, and little hint is given of the incomplete places or the directions in which the developments of the future will be made. Subject to the limitations imposed upon him, the author seems to have done a skillful piece of work, and in this country the book will be very useful for reference, or even for instruction, if supplemented by lectures or other reading.

P. W. BRIDGMAN

The Collected Works of J. Willard Gibbs. Edited by WILLIAM RAYMOND LONGLEY AND RALPH GIBBS VAN NAME. Pp. Vol. I. 434, Vol. II 207+284. Longmans, Green and Company, New York, 1928. Price $6.00 a set.

Appreciation of the fundamental importance of the work of Gibbs has increased rather than decreased since his death, so that this reprint of his work will be most welcome. These two volumes constitute the only complete collection of all the writings of Gibbs; there is, however, nowhere in the two volumes any material that has not already appeared somewhere in print, so that no critical comment on the subject matter is called for by this review. The first volume contains, in addition to a biographical sketch by H. A. Bumstead reprinted from the edition of 1906, all the papers on thermodynamics, of which that On the Equilibrium of Heterogeneous Substances is the most important. The second volume is in two parts. The first of these is a reprint of the Elementary Principles in Statistical Mechanics, which was originally published as a separate volume, and was therefore not included in the 1906 edition of the Collected Works, but which is now out of print; all the present emphasis on statistical theory makes it most desirable to have it again available. The second part contains papers on dynamics, vector analysis and multiple algebra, electromagnetic theory of light, and a half dozen miscellaneous short papers.

In the interest of economy the photographic method of reproduction has been used. The technique of this method has been very skillfully handled, so that, except for a difference in the size of the letters in the parts from different original sources, no one would suspect that it had not all been printed from freshly set type.

P. W. BRIDGMAN

Introduction to Modern Physics. F. K. RICHTMYER. Pp. 596, figs. 169. McGraw-Hill Book Company, New York, 1928. Price $5.00.

By the way, what is modern physics, anyway? Is it the physics of e, m, h, c, and that very modern and elusive quantity called ψ? Does it include also the airplane and the electric dish-washing machine? Does it include Newton, Galileo and Archimedes? To be sure, these questions are of taste, rather than of fact; but so is the question, Shall I read this book?

Here, quite rightly as it appears to the reviewer, the airplane and the dish washer are omitted. For very different reasons, presumably, there is no mention of ψ, or even of its closest experimental companion, the reflection of electrons by crystals. This also may well be quite right: the reviewer, to be sure, would rather see ψ included, even though it is still undergoing discontinuous changes with time, on the emission of quanta of literature; but the author is more cautious, and contents himself with a severe warning against any literal acceptance of theories of electronic orbits.

Whether the general policy exemplified by this point is too conservative or not, one fact is sure: caution of this sort carries with it many virtues. One of these is the ability to make certain that every term is clearly and unambiguously defined, before using it—as ψ, above, is not. Another is the ability to decide what grade of mathematics to assume in the reader—in this case, elementary calculus—and then to stick to it in spite of all temptations. Closely related to that is the patience to go slowly in the development of an abstruse idea, building it up by steps, neither too high nor too low for a student with moderate perseverance and the grade of reasoning ability that can be expected to accompany elementary calculus. Finally, there is good, well-balanced judgment in the selection of topics.

This last point brings us back to the question, does modern physics include Galileo? Well, what would Galileo have said, if someone had asked him, during one of his controversies, "Is your work up-to-date?" The essence of modernism is not existence in the twentieth century, but rather a type of mental activity, progress in the evolution of intellectual processes. Who typifies that better than Galileo? Therefore, who, or what, better deserves a place in an introduction to modern physics?

The parts of history that are of the greatest value to the student who hopes to take an active part in further intellectual evolution, are of course the stories of the evolution already accomplished. Stories with heroes, they are, necessarily, and if written well, they must be written under the inspiration of their subjects. It is hard to be impartial in writing history of this type, and indeed one may well say it is impossible to entirely avoid exaggerating the wisdom of the heroes and the malevolence of the villains. Here, fortunately, the same qualities we have seen elsewhere in the book are active, and the result is a most excellent series of historical chapters, constituting an especially valuable contribution to the introductory literature of modern physics.

D. L. WEBSTER

Wien und Harms Handbuch der Experimentalphysik. Vol. 13/II. Part 1, Physik der Glühelektroden by W. SCHOTTKY AND H. ROTHE. **Part 2, Herstellung der Glühelektroden** by H. SIMON. **Part 3, Technische Elektronenröhren und Ihre Verwendung** by H. ROTHE. Pp. 492, figs. 179. Akademische Verlagsgesselschaft m.b.H., Leipzig, 1928. Price bound 46 RM, unbound 44 RM.

This volume of the Handbuch will be found to be of great value to anyone who is interested in the science or in the art of making or using vacuum tubes. The authors have made valuable contributions to the respective fields which they review. They consequently can and do speak authoritatively and with first hand experience. The greater part of the work consists of a thorough-going and orderly review of all important articles in the literature up to the early part of 1928. The spirit of the original articles is preserved as much as it is possible to do so and still weld the literature into a continuous presentation. The descriptions of the original articles are so complete that the need of referring to the originals will occur only rarely. The authors have gone one step farther and have compared the results of different workers and given a critique of experimental methods and the results obtained. In this respect, however, they have not gone as far as might be desirable. To their credit it should be said that they treat foreign and German publications about equally well. The different parts of the volume are well blended together so that there is practically no duplication. The printing and figures are good.

The presentation of the physics of hot electrodes includes historic survey, thermodynamic and kinetic treatment of electron emission, ionization on hot surfaces, thermionic heating effects contact potentials and thermo-electricity, atomic surface films, behavior of complex substances, movement of electrons in vacuum, image and atom fields, statistical effects. All of these are handled in a masterly fashion. The part on the construction of hot cathodes includes different kinds of hot cathodes and their construction, material and arrangement of electrodes, evacuation methods and temperature determination. The third part on technical vacuum tubes and their use includes thermionic emission and technical vacuum tubes, vacuum tubes as amplifiers, oscillators, and rectifiers.

JOSEPH A. BECKER

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE PASADENA MEETING, DECEMBER 8, 1928

The 154th regular meeting of the American Physical Society was held in the Auditorium of the Norman Bridge Laboratory at the California Institute of Technology, Pasadena, California, on Saturday, December 8. The program consisted of 35 papers, three of which—Nos. 18, 19 and 23—were read by title. Abstracts of these papers are given in the following pages. An AUTHOR INDEX will be found at the end.

L. B. LOEB

Local Secretary for the Pacific Coast

ABSTRACTS

1. Analysis of the gradual oxidation prior to ignition of fuels in internal combustion engine and the relation of such oxidation to detonation. W. M. ZAIKOWSKY, H. B. HOLROYD AND V. M. SOKOLOFF, California Institute of Technology.—A study was made of the change in oxidation of gasoline-air mixture prior to ignition in the engine due to the admixture of 0.25 percent of lead tetra-ethyl. Non-doped mixture was found to undergo a greater oxidation. The difference is equivalent to 2 percent of the total oxygen present in the air-cooled engine. No increase of the compression pressure corresponding to such difference in oxidation was observed, what suggests oxidation is not homogeneous reaction. Study of oxidation of pure and doped gasoline-air mixtures in heated tubes was made. It was found that ethyl lead and other dopes reduce the rate of oxidation of gaseous explosive mixture in gaseous phase during a short time only, while oxides deposited on the tube walls remain continuously effective anti-oxidants. For the solid carbon, lead oxide is found to be distinctly a positive surface catalyst, in addition to the known fact that it is capable of oxidizing hydrogen and light hydrocarbons at relatively low temperature. The effectiveness of antiknock compounds is ascribed to the temporary elimination by them of O_2 molecules sufficiently activated to react with hydrocarbons directly and in this manner reducing activation of the initial products of oxidation of fuel molecules oxidized by the oxygen consumed by the antiknock.

2. Ionization of neon and argon by positive ion bombardment. RICHARD M. SUTTON, Norman Bridge Laboratory, California Institute of Technology.—In a tube of special design, positive ions of potassium from a Kunsman catalyst source were directed into neon or argon at various pressures. By variation of the accelerating potential, evidence of ionization of the gases by the positives was obtained commencing at approximately 100 volts. Definite variation of the effect with change of pressure was noted. Ionization was readily separated from secondary effects of emission of electrons from metal surfaces and reflection of positive ions; such secondary effects did not amount to more than 5 percent of the observed ionization. The number of new ions formed per positive ion impact is decidedly less than for electrons of the same kinetic energy. Attempts to ionize hydrogen by this process gave practically negligible results up to 750 volts, agreeing with the results of W. J. Hooper. Ballistic considerations show that a sharp ionization potential is not to be expected by this method of excitation.

3. The photoelectric effect of liquid tin and two of its allotropic modifications. ALEXANDER GOETZ, California Institute of Technology, Pasadena.—The photoelectric emission of pure tin is measured over a range of temperature from 550° to room temperature. The red limit of the emission was observed to be considerably different for the liquid and the crystalline phase which indicates a qualitative parallelism with the change of the thermionic work function at the melting point of other metals. (A. Goetz, Zs. f. Phys. **42**, 329; **43**, 531, 1927.) Besides this change which goes together with a large decrease in intensity, there is also observed an alteration in the photoelectric threshold at the transition of the tetragonal (β) tin into the hexagonal (γ) tin. For each phase the photoeffect appears to be independent of temperature as long as one corrects the observed values for the change of the optical reflectivity with temperature. The photoelectric thresholds for the different phases as observed are: Tin liquid (232°–550°), 2925 ± 10A; γ-tin hexagonal (203°–232°), 2820 ± 10A; β-tin tetragonal (70°–150°), 2740 ± 10A. The transition from β-tin into γ-tin is found to be remarkably slow and shows an analogy to the well-known small transition—speed of the other allotropic change—β-tin into α-(gray) tin. This explains probably the discordant data of earlier authors who give—assuming the transition is like in other metals a sudden one—the temperature of the allotropic change between 203° and 100°.

4. The ionization of Cs vapor by light of frequency greater than the series limit. ERNEST O. LAWRENCE AND N. EDLEFSEN, University of California.—Using the space charge method of Foote and Mohler [Phys. Rev. **27**, 37–50, (1926)] we have studied the ionization of caesium vapor by light of wave-lengths from the series limit to 2200A. We find that the ionization efficiency of the light falls off rapidly from the series limit to shorter wave-lengths, excepting for wave-lengths near 2536A (Hg line) where the efficiency is of the same order of magnitude as that of the series limit—in agreement with the observations of Foote and Mohler. However, the ionization efficiencies for wave-lengths on either side of 2536A are a great deal less than that of the Hg line, and therefore Foote and Mohler's extrapolation of the ionization efficiency to shorter wave-lengths is not valid. It is probable that the anomalous ionization by light of 2536A is due to the presence of a trace of Hg vapor. Williamson [Phys. Rev. **21**, 107 (1923)] and Lawrence [Phil. Mag. **50**, 345 (1925)] concluded that the ionization efficiency of light in potassium vapor increases rapidly to shorter wave-lengths. Recently Williamson [Proc. Nat'l Acad. **14**, 793 (1928)] has confirmed this conclusion. It appears therefore that caesium and potassium are not similar in behavior.

5. Momentum of photoelectrons in relation to the momentum of the ejecting x-rays. CARL D. ANDERSON, California Institute of Technology.—Photoelectrons ejected from a gas by x-rays have been studied by means of a Wilson cloud chamber. The κ rays of molybdenum and tungsten were employed and tracks obtained in air, hydrogen, argon and a mixture of hydrogen and argon. The momentum of the radiation was found to equal that of the photoelectrons if the average value of their forward components was taken as a measure of their momentum. This is in contradiction to the conclusions of Williams (Nature, **121**, 134 (1928)) and Auger (Compte Rendus, **186**, 758 (1928)) who find the momentum of the photoelectrons to exceed that of the radiation by 20–50 percent. The momentum, however, as calculated from the position of the peak of the longitudinal distribution curve is, in general, greater than the momentum of the incident radiation in agreement with the conclusion of Williams and Auger.

6. Probable values of the general physical constants. RAYMOND T. BIRGE, University of California.—A critical study of existing data yields, $c = (2.99796 \pm 0.00004) \times 10^{10}$ cm·sec^{-1}; $G = (6.664 \pm 0.002) \times 10^{-8}$ dyne·cm^2·g^{-2}; liter $= 1000.027 \pm 0.001$ cm^3; $H = 1.00777 \pm 0.00002$; $He = 4.0022 \pm 0.0004$; $Ag = 107.880 \pm 0.001$; int. ohm $= (1.00051 \pm 0.00002)$ abs. ohm; int. amp $= (0.99995 \pm 0.00005)$ abs. amp; $A_n = (1.013249 \pm 0.000003) \times 10^6$ dyne·cm^{-2}; $A_{45} = (1.013199 \pm 0.000003) \times 10^6$ dyne·cm^{-2}; $v_n = (22.4141 \pm 0.0004) \times 10^3$ cm^3·mole^{-1} $= (22.4135 \pm 0.0004)$ l·mole^{-1}; $T_0 = 273.18 \pm 0.03$°C; $J_{15} = 4.1852 \pm 0.0006$ abs. joules; $J_{20} = 4.1813 \pm 0.0006$ abs. joules; $J'_{15} = 4.1835 \pm 0.0007$ int. joules; $J'_{20} = 4.1796 \pm 0.0007$ int. joules; $F = 96489 \pm 5$ abs. coul. $= 96494 \pm 1$ int. coul; $e = (4.770 \pm 0.005) \times 10^{-10}$ abs. *es* units; e/m (spectroscopic) $= (1.761$

$\pm 0.001) \times 10^7$ abs. *em* units; e/m (deflection) $= (1.769 \pm 0.002)$; $h = (6.547 \pm 0.009) \times 10^{-27}$ erg·sec. Each constant is independent of those following, but may depend on those preceeding. Original results have been recalculated where necessary, using all auxiliary constants as here adopted.

7. Another attempt to find directional effects in cosmic rays. R. A. MILLIKAN AND G. H. CAMERON, California Institute of Technology.—With much improved technique and conditions of observation we have studied anew the intensity of the cosmic rays as a function of orientation with respect to celestial objects without bringing to light the slightest evidence of the existence of a directional effect of any kind. We conclude that if there be any directional effect at all it cannot produce a variation of more than two or three percent at the most in the intensity of the radiation in question.

8. Ion mobilities using the Erikson method on gases of controlled purity. JERRY J. MAHONEY, University of California. Introduced by Leonard B. Loeb.—Measurements of mobilities of ions in air and in air mixed with known quantities of other gases were made, using the Erikson air blast method under conditions where the nature of the purity of the gas could be reasonably controlled. The results show that there is no ageing effect in air dried over P_2O_5 and liquid air, or even in air passed slowly over $CaCl_2$. In these two cases the normal positive and negative ionic mobilities are observed. If air from the room of 60 percent or 90 percent relative humidity at 20°C is used the well known ageing effects of Erikson are observed. With mixtures of 5 percent and 25 percent HCl no ageing effects are observed. With 5 percent NH_3 the positive ion has the same mobility as the negative ion, but at ages over about 0.01 seconds both negative and positive ions show an apparent ageing, the positive ion going over to the usual value observed while the negative ion forms an ion having a mobility between the old and new positive ions. In pure C_2H_2 positive and negative mobilities were observed in agreement with those found by Loeb and Du Sault and Wahlin, while in dry air with 5 percent C_2H_2 normal air mobilities were observed with no ageing effect. It is concluded that the ageing of positive ions in general proceeds very much more rapidly than Erikson assumes and possibly consists in the attachment of the initial positive ion to a bulky molecule of some impurity present. Water vapor and NH_3 inhibit this action.

9. A direct measurement of recombinations of ions and of ions and electrons by a modified alternating field method. LAURISTON C. MARSHALL, University of California. Communicated by Leonard B. Loeb.—In analogy to the alternating field method for measuring ionic mobilities a method has been designed in which by a rotating sector a flash of x-rays in a nearly parallel beam from a 100 kv d.c. set is passed through the ionization chamber. At a varied time interval thereafter the ions are swept out by a high potential d.c. field and the charge is measured for a given number of cycles. This enables recombination to be measured over time intervals of from 5×10^{-4} seconds to 10 seconds and for computed ion concentrations from 10^7 ions/cm^3 to 10^4 ions/cm^3. Results on carefully dried air give the coefficient α as closely 7.5×10^6 which is nearly constant over time and concentration. The method is being applied to pure N_2 and H_2 where electrons are free for appreciable time intervals.

10. A study of the attachment of free electrons to neutral molecules in air and oxygen. AUSTIN M. CRAVATH, University of California.—The fraction h of the collisions between electrons and neutral molecules which result in attachment of the electron to form a negative ion has been measured throughout a considerable range of field strength and pressure in air and oxygen. A new and simple method was used which consisted in pulling electrons a given distance through the gas by means of an electric field, and then measuring the fraction still unattached by means of a grid having a high frequency alternating electric field between the adjacent wires. This grid removes the electrons, but permits the ions to pass through. From the fraction of the electrons still free and the electron mobility data of Townsend and Tizard, h was then calculated. In oxygen, h had a minimum at 0.9 volts average electronic energy and increased with either increase or decrease of the energy from this value. At constant energy, pressure had little effect. In air, h also rapidly increased as the electronic energy was reduced

below 0.9 volts. This was the highest value at which reliable measurements were made. The variation with electron energy and the order of magnitude of the results ($h = 10^{-6}$) are in agreement with Bailey. On the other hand, a rapid variation of h with pressure was found, while according to Bailey a change of pressure at constant electron energy has no effect. New and more direct proof of the permanence of the negative ions in weak fields, and evidence for the detachment of electrons from negative ions in high fields were also obtained.

11. The effects of an homologous series of amines on the mobilities of ions in hydrogen gas. LEONARD B. LOEB AND KARL DYK, University of California.—In discussion of the action of NH_3 gas on the mobilities of positive ions in H_2 gas and air Professor C. A. Kraus suggested that a study of the effect of primary amines might be of considerable interest. Studies of the mobilities in reasonably pure methyl amine CH_3NH_2 and *n*-propyl amine CH_3-CH_2-CH_2NH_2 have been made. The mobility in pure methyl amine is 0.49 cm/sec per volt/cm for the positive ion and 0.54 cm/sec per volt/cm on the old accepted basis, that in pure propyl amine at 75 mm reduced to N.T.P. is 0.24 cm/sec per volt/cm for the positive ion and 0.26 cm/sec per volt/cm for the negative ion. An addition of 0.27 percent of the methyl amine reduces the mobility of the positive and negative ions in H_2 from 5.94 cm/sec and 9.15 cm per sec. to 5.90 cm/sec and 6.66 cm per sec for positive and negative ions respectively. This is in excess of the amount which the Blanc law of mixtures leads one to expect. In *n*-propyl amine the effect is even more striking for 0.26 percent of the amine in H_2. The values here fall from 6.38 cm/sec and 8.37 cm/sec to 3.77 cm/sec and 4.67 cm/sec. This indicates definite attachment of the amines to both ions in which the increased bulk of the molecules decreases the mobility markedly. In NH_3 the negative ion is affected just as in Blanc's law while the positive ion is *increased* in mobility to nearly the value of the negative ion.

12. Intensity measurements in the line spectrum of helium. W. C. MICHELS, California Institute of Technology.—By means of the photographic method described by Hodges at the Pomona meeting of the society, he and the author made a series of measurements on the intensities in the helium spectrum. The spectrum was emitted by a capillary discharge tube, excited by alternating current, at nine pressures, ranging from 1.92 mm to 34.3 mm of mercury. The absolute intensities of the thirteen lines measured show a maximum in the neighborhood of 2 mm to 5 mm pressure, dropping off rapidly below this and more gradually above. The position of this maximum shifts to lower pressures as we go to higher initial energy levels. As no correlation between these results and existing theory was apparent, the author, after modifying the method, has continued the work, with the spectrum excited by the controlled emission from a tungsten filament, in an attempt to isolate the affect of pressure variations from that produced by variations of the electron velocities at the time of impact.

13. O and N spectra in the extreme ultra-violet. D. C. SHELDON, Physical Laboratory, University of California. Introduced by F. S. Brackett.—By use of the method of grazing incidence with a concave speculum metal grating, spectra were observed for *O* and *N* down to 225A. A disruptive discharge through a π shaped discharge tube was used as a source. The plates were placed between the grating and the central image thus giving a very great dispersion. The dispersion increases with the wave-length from about 1.80 Angstroms per mm at 200A, to 1.25 Angstroms per mm at 450A.

14. The heat of dissociation of nitrogen. JOSEPH KAPLAN, University of California at Los Angeles.—Evidence is presented favoring a value of less than 9.1 volts for the heat of dissociation of nitrogen. The present argument is based on the assumption that the total energy in the D level of the molecule is only slightly greater than the energy in the D_0 level. The justification for this assumption is the absence of transitions other than the $D_0 - B_n$ transitions which arise when the fourth positive group is emitted. The energy of the molecule in the D_0 level is 14.8 volts so that a reasonable value for the total energy in the D level would be less than 15.0 volts. Making the statement that the products of dissociation in the D level are a nitrogen atom in the ^2D state and one in the ^2P state the resulting value for the heat of dissociation is 9.1 volts. The energy in the ^2D level is 2.4 volts and that in the ^2P level is 3.5 volts. If the

total energies in the X' and A' levels of the molecule ion are calculated from this heat of dissociation they are found to be 26.0 and 23.6 volts respectively. The average of the observed values are 26.0 and 23.7 volts.

15. Revision of a former value of the specific charge of an electron, e/m. HAROLD D. BABCOCK, Mount Wilson Observatory.—In 1923 the ratio e/m was determined from the Zeeman effect produced on 116 spectral lines by magnetic fields of measured intensity. The result depended chiefly on lines well adapted to the purpose, but, due to lack of theoretical criteria for the selection of lines, some were occasionally used which are now known to be unsuitable and others which are not yet identified in multiplets. Recent progress in the analysis of the spectra of Cr and Ti permits a revision of the list of lines and the calculation of a new result free from the small errors formerly included. The weighted mean of 48 determinations is found, after correction for the latest value for the velocity of light, to be $e/m=(1.7606\pm0.0012)\times10^7$ e.m.u./gram, practically the same as the former result, accidentally coincident with the observation of Houston, and very close to the value deduced by Birge, but distinctly lower than the results of most other investigators.

16. Some relationships between singlets and triplets in the spectra of two-electron systems. WILLIAM V. HOUSTON, California Institute of Technology.—The Darwin-Pauli theory of the magnetic electron provides a practical means of calculating the details of complicated spectra by the Schroedinger perturbation method. Applied to the simple case of two electrons in an arbitrary central field with one of the electrons in an s state, this gives the positions of the levels when the singlets and triplets are not widely separated. It is thus possible to predict the position of the singlet when the triplet is known. The consideration of the energy in an external magnetic field gives an expression for the Landé g factor which agrees with the observed values for the cases where the Landé formula is not applicable. Expressions are also derived for the intensity of the intercombination lines, which show that these lines must be included if the sum rules are to be applicable. The intensities of these intercombination lines are roughly inversely proportional to the square of the separation of singlets and triplets, so that the observed intensity is usually due to the metastability of the upper state.

17. On the influence of collisions on the structure of Fraunhofer lines. ALBRECHT UNSÖLD, Mount Wilson Observatory. Introduced by Charles E. St. John.—As H. N. Russell, J. Q. Stewart, and others have shown, the absorption lines of the solar spectrum are mainly produced by resonance scattering. In order to explain the fact that the absorption lines are not perfectly black, but have a certain intensity at their centers, a further assumption is required. One must also take into account the influence of collisions (extinction of the resonance radiation and, as inverse process, thermal excitation). The differential equations of radiative equilibrium take then the most general form given by K. Schwarzschild (1914). For the central intensity I of a line one obtains:

$$I=B\left\{1-\frac{1}{(1/2)\{\lambda+[\lambda(2+\lambda)]^{1/2}\}\{1+(3/2)\cos\theta\}}\right\}$$

B is the Kirchhoff-Planck function for the solar temperature; $\lambda/2$ the number of "extinguishing" collisions per lifetime of the excited state. The application of this theory to an atmosphere whose λ (proportional to pressure) decreases towards the top, explains the observation that in spectroheliographic images the center of a line corresponds to high levels, while the "wings" correspond to lower levels. Our assumptions are also fully confirmed by numerous other observations, such as difference of the lines between center and limb of the sun; differences between the spectra of giant and dwarf stars.

18. Polarization of the L_{β_1} radiation of tungsten. PAUL KIRKPATRICK AND IWAO MIYAKE University of Hawaii.—The radiation investigated was reflected from 210 planes of rock-salt in the first order, at an angle $\theta=30°\ 30'$. The reflected intensity was measured by ionization, with the x-ray tube placed successively in positions parallel and perpendicular to the plane of reflection. From the ratio of these two reflected intensities the polarization of the reflected

radiation may be deduced, as one of us has previously shown (Phys. Rev., 29, 1927). Reflected intensities were measured by sweeping the crystal through the position of reflection and noting the total resultant ionization. Variations in reflected intensity from causes other than polarization were checked out by the use of a separate, stationary ionization chamber receiving the radiation directly transmitted by the crystal. By measuring the polarization of the characteristic line, together with its associated general radiation, and measuring separately the polarization of the general radiation near to the line, it was possible to deduce the polarization of the characteristic radiation alone. A mean of several determinations resulted in the value 1.002 ± 0.017 for the ratio of the mutually perpendicular electric vectorial components of intensity in the L_{β_1} radiation. Within the limits of these observations, therefore, this radiation is unpolarized. The maximum potential applied to the x-ray tube was 70 kilovolts, and the tube current 3.25 milliamperes.

19. The ultra-violet light of the sun as the origin of auroras and magnetic storms. H. B. MARIS AND E. O. HULBURT, Naval Research Laboratory.—It is assumed that the sun, when active, emits a sudden (1/2 hour) blast of ultra-violet light. For example, if 1/10,000 part of the solar surface, normally at a temperature of 6000°, were removed and there were exposed the black-body radiations at 30,000°, the solar constant would be increased by 1 percent (as is observed) and the ultra-violet energy, λ500 to 1000A, by 10^8. This ultra-violet energy, completely absorbed in the high lying (200 km) atmospheric gaseous layers, blasts out these layers to produce ions up to 40,000 km. Due to gravity and the earth's magnetic field the first effect of the high flying ions is to produce a sudden current, 10^6 amperes, in planes parallel to the equator, which causes a magnetic field 10^{-3} gauss simultaneously over the whole earth, as is observed in the first phase of the world-wide magnetic storms. Numbers of ions descend to the zones 23° from the magnetic poles and form there diamagnetic concentrations of considerable intensity (also give rise to the auroras). On the assumption that the blast of ultra-violet light does not die away abruptly but continues with lessening intensity for a day or so, the diamagnetic concentrations wax with the day and wane with the night. The changes in the earth's magnetic field caused by this diamagnetism are found to agree in nearly every detail with the observed complicated diurnal storm variations in the three magnetic field components at all latitudes.

20. What is the moon made of? PAUL S. EPSTEIN, California Institute of Technology.—The writer is indebted to Messrs. Nicholson and Pettit of Mt. Wilson Observatory for admirable observational material on the change of temperature of the moon during a lunar eclipse. Theoretically the decrease of temperature for the initial phase of the eclipse should follow the law $\Delta T = -4At^{3/2}/3t_0(\pi\kappa\rho c)^{1/2}$. A denotes the insolation in the beginning, t the time counted from a moment a few minutes after the setting in of the eclipse, t_0 the duration of the penumbra stage, κ heat conductivity, ρ density, c specific heat of the material of the moon surface. Comparison with Nicholson and Pettit's curve gives for $1/(\kappa\rho c)^{1/2}$ a value in the neighborhood of 120. For terrestrial materials this coefficient has the following values: granite 16, basalt 24, quartz sand 58, cellite 90, pumice stone from 100to 150. It follows that the surface layer of the moon could not be made of any solid rock known on earth but must consist of some highly porous material comparable in its thermic qualities to volcanic ashes.

21. Settling of gases and constitution of the atmosphere. PAUL S. EPSTEIN, California Institute of Technology.—There are two processes going on in the atmosphere: (a) diffusion in the gravitational field of the earth which tends to produce a concentration of each constituent gas according to the barometric law; (b) a violent stirring action due to convection currents. The time element of the diffusion process was investigated; it is controlled by an equation of the type $\partial u/\partial t = a^2 x^{-m} \partial^2 u/\partial x^2$, a complete theory of which was developed. If we start from a state in which the atmosphere contains a small uniform percentage of hydrogen, the time necessary for the hydrogen to come near the equilibrium distribution in the absence of convection currents turns out to be large compared with 10000 years. In a period of 10 years the concentration will not change more than 0.3 percent. For heavier gases the periods involved are still larger. We must conclude that for the lower parts of the atmosphere (troposphere) the

stirring process is the more powerful one, and that their constitution is essentially uniform, apart from local contaminations. Concentrations according to the barometric law will set in at higher levels where the density is too small for vigorous convection.

22. A new treatment of vortex motion. H. BATEMAN, California Institute of Technology. —An investigation in which the component velocities (u, v, w) of a particle of fluid are represented by expressions of type $u=\partial\phi/\partial x-\dot{s}\partial s/\partial x$ where $\dot{s}=ds/dt$ and s and ϕ are functions of x, y, z and t. A generalization of Bernoulli's equation is obtained which, for the case of steady motion, is of type

$$p/\rho+(u^2+v^2+w^2+s^2)/2=\text{constant}.$$

This equation accounts for the losses of head in the wake of an airfoil.

23. On the assumptions of matrix mechanics. BORIS PODOLSKY, University of California. —An investigation of the assumptions of the matrix mechanics shows that it is possible to derive all essential properties of matrices from a single physical assumption. This assumption may be stated as follows: Corresponding to any mechanical system there exists a matrix scheme in which matrices corresponding to dynamical variables satisfy the same equations as the dynamical variables themselves do classically, except that instead of the commutative law of multiplication $xy-yx\equiv(hi/2\pi)[x, y]$, where $[x, y]$ is the usual Poisson bracket expression. The method of constructing these matrices, with the help of certain functions, is derived, and these functions are shown to satisfy Schrödinger differential equation. The properties of the matrices follow: (1) matrices corresponding to coordinates and momenta satisfy the Heisenberg-Dirac quantum conditions; (2) matrices satisfy the equation of motion of Heisenberg's mechanics; (3) in a system with well ordered Hamiltonian matrices of well ordered functions are Hermitian; (4) for a conservative system the matrix of the Hamiltonian is diagonal; and (5) for a conservative system matrix elements have the form $c(a'a'')\exp\{2\pi i[E(a')-E(a'')]t/h\}$ where $c(a'a'')$ is a constant and $E(a')$ and $E(a'')$ are the characteristic values of the energy. This paper may be regarded as a development of Dirac's transformation theory. For a physical interpretation of matrices further assumptions are required.

24. Protonic spin. BENEDICT CASSEN, California Institute of Technology.—It is shown that Dennison's theory of the rotational specific heat of hydrogen is not evidence for assigning spins and antisymmetric wave functions to protons. It is found that his theory in conjunction with evidence obtained from nuclear structure lead to the assignment of symmetric wave functions to protons.

25. Quantum defects for non-penetrating orbits. LINUS PAULING, California Institute of Technology.—The contribution of polarization of the atomic core to the quantum defect for "non-penetrating" orbits of alkali-like atoms and ions has been calculated with the use of the quantum mechanics equation and the known values of the core polarizabilities (Pauling, Proc. Roy. Soc., **A114,** 181 (1927). The calculated values are smaller than the observed quantum defects by an amount which decreases for successive series in the order $p>d>f$, etc., and which increases for isosteric ions with increasing degree of ionization; for example, in the order $Li_I<Be_{II}<B_{III}<C_{IV}$. It is further shown by the application of the first order perturbation theory that even for these orbits penetration of the atom core is not negligible. Values of the quantum defect calculated by taking into account both penetration and polarization of the atom core are in good agreement with those observed.

26. Shot fluctuations in wave mechanics. BENEDICT CASSEN. California Institute of Technology.—It is shown that the Born-Dirac interpretation of the transformation functions of quantum mechanics allows for fluctuations in time in a stationary state but gives no information about these fluctuations. The Schroedinger interpretation excludes such "shot" fluctuations in what Weyl calls a "pure state" so that they can only occur in a superposition of pure states in various phase relationships. It is shown that such superposition of waves can explain shot effects without assuming any inherent fluctuation in a stationary state.

27. Spectral intensities of non-harmonic and aperiodic systems. BENEDICT CASSEN, California Institute of Technology.—A general formula is derived for the intensity of radiation in a quantum jump in any kind of quantum dynamical system. The total energy radiated by s, t jumps is

$$P(s,t)=\frac{2e^2}{3m^2c^2}\left|\int\int\int\left[\left(\frac{\partial V}{\partial x}\right)^2+\left(\frac{\partial V}{\partial y}\right)^2+\left(\frac{\partial V}{\partial z}\right)^2\right]^{1/2}\psi_s^*\psi_t dxdydz\right|^2$$

where V is the potential energy function for the system. For the intensity of s, t radiation in the l, m, n direction we get

$$I_{l,m,n}(s,t)=\frac{e^2}{4\pi m^2\gamma^2c^3}\left[\left|\int\int\int\left[\left(\frac{\partial V}{\partial x}\right)^2+\left(\frac{\partial V}{\partial y}\right)^2+\left(\frac{\partial V}{\partial z}\right)^2\right]^{1/2}\psi_s^*\psi_t dxdydz\right|^2-\left|\int\int\int\left[l\frac{\partial V}{\partial x}+m\frac{\partial V}{\partial y}+n\frac{\partial V}{dz}\right]\psi_s^*\psi_t dxdydz\right|^2\right]$$

The Heisenberg amplitude rule is only strictly applicable to an harmonic oscillator.

28. Relative intensities of multiplets in triads of titanium. GEORGE R. HARRISON AND HARRY ENGWICHT, Stanford University.—The relative total intensities of the multiplets in five triads of Ti I have been measured by photographic photometry, to test experimentally Kronig's formulas for relative intensities of multiplets. In cases where the separation is small so that the ν^4 and excitation corrections can be neglected the formulas are confirmed. For the close multiplets $a^3F'-b^3F$ and $a^3F'-b^3D'$, arising from the configurations $(3d)^2(4s)^2-(3d)^24s4p$, Kronig's theory gives 7:5 for the ratio of intensities, while measurements give 7:4.8, with a probable error of 5 percent. For the triad $a^5F'-b^5G'$, b^5F, c^5D', configurations $(3d)^34s-(3d)^34p$, uncorrected theory gives 9:7:5 and experiment 8.38:7:5.11. When the ν^4 correction is applied the experimental values become 12.2:7:4.22. Applying an excitation correction using that temperature which gives closest agreement we get 9.1:7:5.0 for a temperature of 10,000°K. This is in agreement with the known characteristic of electrically excited sources at low pressures, where the electrons acquire velocities greatly in excess of those corresponding to thermal equilibrium. Analogous results are obtained for the other triads measured.

29. Intensity formulas and the strong multiplets of titanium. GEORGE R. HARRISON, Stanford University.—The relative intensities of the lines in 35 of the strong multiplets of Ti I and Ti II have been measured. Approximately two-thirds of the multiplets obey the intensity formulas and the Sum Rule to within three or four percent. Of the remaining one-third, two-thirds of the lines are normal, while about one-sixth are too weak, and one-sixth too strong. There is a slight predominance of weak lines over strong ones, probably accounted for by the presence of inter-system combinations. Comparison of selected multiplets with homologous ones of neighboring elements, measured by Frerichs, showed no similarity in departures from the formulas, these apparently being characteristic of individual atoms. No correlation between departure from the intensity formulas and from Landé's interval rule and the standard Zeeman patterns were found in titanium. The Sum Rule was violated practically as often as the intensity formulas. Of 250 lines measured, however, 86 percent obeyed the formulas, while 7.6 percent were too weak and 6.4 percent were too strong. Deviations in certain cases were as great as 100 percent, but with no relation to the type of multiplet involved.

30. The theory of diffuse band spectra. O. K. RICE, National Research Fellow, California Institute of Technology.—Suppose we have a wave equation which represents *approximately* the state of a molecule and which has certain eigenfunctions. Then the extra terms in the *exact* wave equation may be treated in the usual manner as a perturbation, and the perturbed eigenfunctions may be expressed as a linear function of the unperturbed ones. In the present paper the case is discussed in which the unperturbed eigenfunctions are of two sorts, some corresponding to a continuous set of states, while some correspond to a discrete set superimposed upon the continuous set. Then the properties of the perturbed eigenfunctions will depend upon the

relative importance, in the linear expression, of the two kinds of unperturbed eigenfunctions. The energy range over which the properties of a given discrete state may wholly or largely determine the properties of the perturbed eigenfunctions is considered on the basis of a modified Schrödinger perturbation theory. There are deduced the properties of the molecular spectrum which results when transitions may occur from some initial state to a final state which is described by the perturbed eigenfunctions considered above. In particular, the conditions under which the band spectrum will be diffuse are considered.

31. Total reflection of x-rays from thin nickel films on platinum. HIRAM W. EDWARDS, University of California at Los Angeles.—In a report of an investigation of the total reflection of x-rays from thin nickel films of different thicknesses (Phys. Rev. **32,** 712 (1928)) sputtered on glass, it was shown by the writer that the critical angle for $\lambda = 0.707$A varied from 0.0016 radians that of the glass support, to 0.0034 radians, the value for normal nickel. Critical angles of less than normal were explained by assuming that the electrons of glass under the nickel film participated in the reflection phenomenon. This conclusion is substantiated by measurements made on thin nickel films sputtered upon thick platinum films. For $\lambda = 0.707$A the critical angle for bare platinum was found to be 0.0040. The thinnest nickel film was found to be greater than this. With increasing thickness of the nickel film the critical angle decreased. Seven films sputtered under similar conditions but with sputtering times of 2, 3, 4, 5, 6, 10 and 50 minutes gave critical angles of 0.0043, 0.0043, 0.0043, 0.0041, 0.0039, 0.0037, and 0.0034 radians respectively. These results seem to give conclusive evidence that reflection of x-rays from nickel is not a purely surface phenomenon but is one which requires a layer of metal of probably definite thickness.

32. The existence of radioactive recoil ions of high mobility in air. LORA LANE LOEB AND LEONARD B. LOEB, University of California.—Using an air blast method Erikson (Phys. Rev. **24,** 622 (1924) and **26,** 629, (1925)) observed positive ions from radioactive recoil atoms of Th, Ac, and Ra emanations having two mobilities, 4.35 cm/sec and 1.56 cm/sec per volt/cm. The relative numbers of the two ions was about equal and did not vary with age. In view of the great difficulty encountered in explaining the faster of these two ions (Science **67,** 468, (1928)) an investigation was undertaken using the ions from recoil atoms of ThC (that is ThC″) with an alternating current method, and a radioactive study of the deposit of ions. For ions crossing 0.5 cm of air in from 0.016 to 0.0006 seconds only ions of normal mobility of about 1.6 to 2.0 cm/sec per volt/cm were observed. In no case was any indication of ions of mobility greater than 2.5 cm/sec per volt/cm observed within the limits of the observations which were certainly better than 5 percent.

33. Heat conduction in crystals from the point of view of wave mechanics. TH. VON KARMAN, California Institute of Technology.—Planck's quantum theory proved adequate to bring the phenomena of *specific heats* into good agreement with experiment. While it was not successful in explaining the data on heat conduction, Debye found that ideal crystal lattices with a linear law for the interaction between the lattice elements (i.e. a system of harmonic oscillators) do not show any phenomenon analogous to heat conduction, and he made an attempt to develop a tentative theory taking into account small deviations from the linear law.

The new quantum mechanics enables us to avoid this difficulty. Consider the simplest model of a crystal: two particles with the potential energy $x_1^2+x_2^2-2x_1x_2$. If we first cancel the term $-2x_1x_2$, we have two independent oscillators with given characteristic functions for Schroedinger's equation. Introducing the term $-2x_1x_2$, as a perturbation of the energy expression in the equation, we get the result that only those states in which the difference of the energies of the two oscillators equals $E_1-E_2=h\nu$ permit energy transfer from one oscillator to the other.

Assuming the energy distribution for the two oscillators to correspond to temperatures T and T', and denoting the probabilities of the energy level $nh\nu$ by $\pi(n)$ and $\pi'(n)$ respectively, we obtain for the energy flow in unit time the expression, $E=(\alpha h/m)\sum_n n^2[\pi(n)\pi'(n-1) - \pi'(n)\pi(n-1)]$. Computing $\pi(n)$ by means of Planck's statistics, we get with $h\nu/kt=\sigma$ and for small temperature differences ΔT

$$E=\frac{\alpha h}{m}\ \frac{1+\tanh^2\sigma/2}{4\sinh\sigma}\sigma\frac{\Delta T}{T}$$

This leads to the relation $E \alpha 1/T$ for high temperatures which is in agreement with experiment, while the energy flow vanishes for low temperatures. If instead of two particles we consider two systems of N particles, connected elastically, we get the same law as above for high temperatures but a constant limiting value for $T=0$. It may be mentioned that the heat conduction of diamond is, in fact, practically constant between $T=0$ and $T=300°$K., i.e. for temperatures which, in the case of diamond, must be considered as very low.

34. The cathode drop in a mercury arc. S. S. MACKEOWN, California Institute of Technology.—By making the assumption that the total cathode drop occurs in a distance less than one mean free path from the cathode, Poisson's equation can be solved. If the experimental values of 4000 amperes per square centimeter and 8.6 volts are used for the current density at the cathode and the cathode drop, values for the electric field existing at the surface of the cathode can be determined for varying percentages of the current carried by positive ions. If 5 percent of the current at the cathode is carried by positive ions, the field existing at the surface of the cathode exceeds 5×10^5 volts per cm. This is probably sufficient to furnish the necessary electron current by "field" currents produced by this high field. The whole cathode drop occurs within a distance of approximately 2×10^{-3} centimeters, so that the original assumption is justified.

35. Lunar radiation and temperatures during an eclipse. EDISON PETTIT AND SETH B. NICHOLSON.—Measurements of planetary heat from a point on the moon 2′ from the south limb were made with the thermocouple and microscope cover glass screen attached to the 100-inch telescope during the lunar eclipse of June 14, 1927, The planetary radiation during the partial phase of the eclipse lasting an hour followed nearly the formula $h=(0.44H+0.17)$ cal cm^{-2} mm^{-1} where h is the heat radiated by the moon and H is the heat received by it from the sun.

During totality which lasted $2^h\ 40^m$ the equations became

$$h=(0.065-83t\times10^{-6})\text{ cal cm}^{-2}\text{ mm}^{-1}$$

where t is the minutes elapsed beginning a half hour after totality. For 20 minutes after totality the radiation does not change much, but then begins to rise rapidly according to the formula

$$h=(1.1H-0.81)\text{ cal cm}^{-2}\text{ mm}^{-1}.$$

The temperatures corresponding to these formulae are about 346°K at the beginning of eclipse, 210°K at the beginning of totality and 152°K at the end of totality.

From these data 1.1 cal cm^{-2} mm^{-1} is absorbed but reradiated, 0.1 cal cm^{-2} mm^{-1} or six percent of H is conducted into the surface before eclipse, and about 0.044 cal cm^{-2} mm^{-1} is conducted out of the surface at the end of the total phase.

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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE NEW YORK MEETING, DECEMBER 27, 28, 29 AND 31, 1928

The Thirtieth Annual Meeting (the 155th regular meeting) of the American Physical Society was held in New York City, Thursday, Friday, Saturday, and Monday, December 27, 28, 29 and 31, 1928. The presiding officers were Professor Karl T. Compton, President of the Society, and Professor Henry G. Gale, Vice-President. The average attendance was about 350.

The annual joint session with Section B was held on Friday afternoon at the American Museum of Natural History. The presiding officer was Professor P. W. Bridgman, Vice-President of Section B. The program consisted of an address by Dr. W. S. Adams of the Mount Wilson Observatory on "A Large Telescope and its Possibilities" and an address by Dr. W. J. Humphreys of the U. S. Weather Bureau on "Samples of Outdoor Physics."

The address of the Retiring Vice-President of Section B., Professor Arthur H. Compton, was delivered as the Sigma Xi address on Friday evening. Preceding the address there was a joint dinner of the Sigma Xi Society and the American Physical Society attended by 387 persons.

On Monday there was a joint session of the American Physical Society and the American Mathematical Society consisting of a Symposium on Quantum Mechanics, with an attendance of about 400. The principal addresses were by Professors J. C. Slater, J. H. Van Vleck, H. Weyl, and N. Wiener. In addition there were a number of short ten minute papers.

Annual Business Meeting. The regular annual business meeting of the American Physical Society was held on Saturday morning, December 29, at eleven o'clock. A canvass of the ballots for officers resulted in elections for the year 1929 as follows:

President:	Henry G. Gale
Vice-President:	W. F. G. Swann
Secretary:	W. L. Severinghaus
Treasurer:	George B. Pegram

Managing Editor of the Physical Review, Three-year term:
John T. Tate

Members of the Council, Four-year term:
Herbert E. Ives Alfred L. Loomis

Members of the Board of Editors of the Physical Review, Three-year term:
Edward U. Condon C. J. Davisson F. K. Richtmyer

The Secretary reported that during the year there had been 307 elections to membership. The deaths of 15 members had been reported during the year, 27 had resigned and 19 had been dropped. The membership of the Society on December 29, 1928 was as follows: Members, 1637; Fellows, 520; Honorary Members, 6; Total Membership, 2163. The numbers are approximate because they include elections and transfers at the November and December meetings. In the year there had been a net increase of 191 members, a net increase of 55 fellows and a decrease of 1 honorary member.

On motion the Society passed a resolution expressing its thanks to the retiring Secretary for his services during the past six years.

Meeting of the Council. At its meeting held on December 27, 1928 the Council adopted a minute expressing regret at the death of Professor Alfred Dodge Cole and recognition of his services as Secretary from 1913 to 1918.

The following resolutions were adopted:

1. That the Society authorize the publication of supplements to the Physical Review, these to contain resumés, discussions of topics of unusual interest and, in a broad sense, material that will give valuable aid to productive work in physics and yet that cannot appropriately be published in the Physical Review.

2. That the editor of these supplements be the Editor of the Physical Review and that there be an advisory editorial board to be appointed by the President upon the recommendation of the Editor.

3. That the Society assume the financial responsibility for the issuance of 300 pages in 1929 and for more pages if funds other than those of the Society can be secured for the purpose.

4. That the subscription to these supplements be separate from that of the Physical Review and be not included in the membership fee at present.

Professor Leonard B. Loeb was appointed Local Secretary for the Pacific Coast Section for 1929.

Four persons were elected to Fellowship, six persons were transferred from Membership to Fellowship, and fifty-two were elected to Membership. *Elected to Fellowship:* Alexander Goetz, Charles A. Kraus, Charles Sheard and Hermann Weyl. *Transferred from Membership to Fellowship:* H. E. Farnsworth, Ertle L. Harrington, Alfred L. Loomis, Morton Masius, W. J. Pietenpol and Oscar K. Rice. *Elected to Membership:* Gabrielle Asset, P. M. S. Blackett, Julian M. Blair, Emily H. Boggs, J. Lloyd Bohn, Ralph K. Bonell, E. Milton Boone, Francis H. Bowen, Louis F. Brown, Willoughby M. Cady, A. Dixon Callihan, G. Harvey Cameron, V. L. Chrisler, Robert B. Corey, C. L. Cottrell, W. Robert Couch, Richard B. Dow, Theodore Dunham, Jr., W. E. Gordon, Robert J. Havighurst, Harold Heins, Dorothy Heyworth, J. P. Jacobson, Merton W. Jones, Marie Kernaghan, L. Merle Kirkpatrick, Louis Malter, H. Artis Miley, Harry R. Mimno, Leo Nedelsky, D. E. Olshevsky, Harry F. Olson, Lars Onsager, Clarence J. Overbeck, R. V. Parsons, Dixon B. Penick, George E. Read, J. K. Roberts, Arthur L. Samuel, Louise A. Schwabe, Harold H. Scott, Gayle Shirey, Maynard P. Shoemaker, Howard P. Stabler, Wesley Stein, Doris Thomas, Richard Tousey, M. A. Tuve, Newton Underwood, Dorothy W. Weeks, Everett C. Westerfield, E. Russell Wightman.

The regular program of the American Physical Society consisted of 70 papers, Numbers 1, 10, 40, 42, 45, 52 and 70 being read by title. The abstracts of these papers are given in the following pages. An AUTHOR INDEX will be found at the end.

HAROLD W. WEBB, *Secretary*

ABSTRACTS

1. The surface tension of mercury in the presence of gases under varying pressures. S. G. COOK, Washington University. (Introduced by G. E. M. Jauncey.)—Quincke's method with Worthington's correction (Pogg. Ann. **139**, 1 and Phil. Mag. (5), **20**, 51 (1885)) was used. Contrary to the accepted values the maximum surface tension of mercury, (515 ± 7 dynes/cm at 31°C) is reached when only mercury vapor is present. A surface freshly created in a gas at 760 mm has a high initial tension approaching that when the surface is created in mercury vapor. The tension falls as the gas is adsorbed until an equilibrium value for a given pressure is attained. As the pressure is reduced the equilibrium value rises to a maximum which depends upon the nature of the gas. For instance, this maximum tension for mercury-hydrogen occurs at the critical pressure of 2.8 mm. If the pressure is lowered to stiction the tension remains unchanged so long as the mercury is not agitated beyond a certain amount. This maximum value for mercury-hydrogen is 442 dynes/cm which is less than the mercury-mercury vapor value of 515 dynes/cm. If the mercury- hydrogen is violently agitated when the pressure has been reduced to stiction the tension approaches 515 dynes/cm, the mercury-mercury vapor tension.

2. Internal friction in metals. R. H. CANFIELD, Naval Research Laboratory.—Further experiments using the author's method (Phys. Rev. **32**, 3, (1928)) have been made on copper and iron to determine the effect of grain-size, cold work, and other physical factors, on the coefficient of internal friction and other features of the dissipation curve.

3. Photographic observations of ballistic phenomena. L. THOMPSON AND N. RIFFOLT, Dahlgren, Va.—The subject records were obtained in a photographic study of the development of secondary explosion and the propagation of gases subsequent to ejection from large caliber guns; of the motion of a projectile during the penetration of armor; of bursting projectile in flight, by single exposure method; velocity data by trace on stationary film; measurement of long time intervals using an oscillographic modification of a high speed motion picture camera and series of electrically controlled high frequency indicators; application to the determination of velocity and time of fall, burst ranging data, and to the study of operations requiring precise evaluation of periods of considerable duration.

4. The effect of temperature treatment on the establishment of a stable condition of the electrodes in a polarization cell. E. E. ZIMMERMAN, Cornell University.—If measurements of the value of polarization capacity of a cell having freshly polished plain platinum or gold electrodes are made soon after the electrodes are inserted, it is found that successive measurements may give widely different values of capacity, especially in the case with platinum electrodes. It has been found that by a process of temperature treatment of the cell, in which the temperature is increased through a range from 0°C to 90 or 95° and then decreased through the same range, with probably one or two repetitions of the procedure, the electrodes are brought to a condition corresponding to minimum capacity. During the process of treatment, the polarization capacity decreases from 10 to 40 percent and the polarization resistance increases by a similar amount. Curves are given showing the manner in which the polarization capacity and resistance change during process of treatment. This method of reducing the electrodes to a stable condition is more effective and requires much less time than the method of leaving the electrodes shorted and in the solution for several hours.

5. A new theory of the rectifying action of the aluminum cell. W. B. PIETENPOL AND A. P. FRIESEN, University of Colorado.—The oxide layer-gas film theory has been largely accepted

for the valve action of the aluminum cell. (Guthe; Gunther-Schulze; Fitch; Meserve.) Previous investigators differ as to the relative importance of the oxide layer and the gas film formed on the aluminum anode in explaining the electrical characteristics of the cell. Much experimental evidence has convinced the authors that the oxide-gas film theory is not satisfactory and a modified theory is proposed. Aluminum when exposed to air has a thin oxide layer on its surface. In contact with an electrolyte like sodium bicarbonate a gelatinous hydrate is formed. The behavior of the cell is attributed to a double layer, aluminum oxide and aluminum hydroxide. The hydroxide layer acts as a semi-permeable membrane to certain ions. The accumulation of negative ions in this layer when aluminum is the anode accounts for the high resistance and the counter electromotive force observed. To this double layer likewise is attributed the capacity of the cell. The thickness of the gelatinous hydroxide layer depends upon the rate at which aluminum oxide is formed and the rate at which aluminum hydroxide goes into solution. With time of applied d.c. voltage ultimately an equilibrium condition is reached. On the present theory the oxide layer decreases in thickness with time of open circuit. The current-time relationship found by Meserve (Phys. Rev. **30**, 215, (1927)) is shown to be limited.

6. Equilibria in systems with surface phases. N. RASHEVSKY, Westinghouse El. & Mfg. Co., East Pittsburgh, Pa.—It is shown by thermodynamical considerations, that in a system which contains a monomolecular surface-phase at the boundary surface, and in which the surface energy is comparable to the volume energy, the free energy of the system depends not only on the total masses of the components and the volume, but also on the area of the boundary surface. For a given mass and volume of the system, there is a definite value of this area, for which the free energy has a minimum, and which corresponds to the stable equilibrium of the system. For this value of the area the capillary pressure vanishes, and thus a free liquid system, not subject to gravity, may acquire a non-spherical shape. The case is observed on myelinic formations. Furthermore, the modifications of the phase-rule, due to not neglecting the surface energy, are investigated.

7. Orientation of crystals in magnetic fields. DIMITRY E. OLSHEVSKY, University of Pittsburgh. (Introduced by A. G. Worthing.)—The statistical orientation of small crystals exposed to strong magnetic fields has been studied theoretically and experimentally. The problem of orientation of a single crystal suspended in a viscous liquid is treated first, including the influence of the Brownian movement. The statistical problem of orientation for a microcrystalline suspension is then studied on the basis of (a) elementary laws developed for a single crystalline particle, and (b) thermodynamical considerations. Lastly, the problem of a growing particle is treated and the probability function of orientation for a crystalline deposit at the bottom of a container is deduced. Both the three dimensional probability function and its orthogonal projection (observed from a distant point) are found. Quantitative experimental work has been carried out particularly with basic sulphate of iron and ammonium with field intensities of 13500 gausses. Distribution curves of orientation were obtained from 160 individual crystals. Two cases of orientation are found corresponding to the hexagonal bases of the prismatic crystals (1) approximately parallel to plane of deposit (2) approximately perpendicular to it. In the first case the distribution function has six major and six minor maxima, the former corresponding to first order crystallographic axes. The existence of discrete orientations for the elementary magnets is suggested. In the second case the distribution function has two maxima in agreement with theory.

8. Some electromechanical properties of Rochelle Salt crystals. W. G. CADY, Wesleyan University.—Up to the present time the values of the piezo-electric strain-constants δ of Rochelle salt have been known, but not those of the moduli ϵ. The writer has now computed the latter from Pockels' values of the strain-constants ($\Delta_{14}=10^{-8}$, $\delta_{25}=-165\times10^{-8}$, $\delta_{36}=35\times10^{-8}$) together with the elastic constants as recently determined by Mandell (Proc. Roy. Soc. A. **116**, 623, (1927)). The resulting values are $\epsilon_{14}=1.64\times10^{8}$, $\epsilon_{25}=-53{,}300$, $\epsilon_{36}=43{,}400$. From the δ's and ϵ's the extent to which the dielectric constant k is modified by the presence of piezo-electricity in the case of Rochelle salt has been computed, completely explaining the very large value of k found by Valasek (Phys. Rev. **19**, 478, (1922)). On the experimental

side, the natural vibration frequencies of many Rochelle salt plates variously oriented with respect to the crystal axes were measured. Fair agreement was found with the frequencies computed from Mandell's elastic constants. When plates having their edges parallel to the crystallographic axes are placed in an alternating electric field of suitable frequency, resonant vibrations are set up which are not of compressional type, but due to stationary systems of shear, or transverse, waves (waves of distortion).

9. Modulation of light waves by high frequency radio waves. A. BRAMLEY, Fellow, Bartol Research Foundation of the Franklin Institute.—The light from an iron arc was passed through a parallel plate Kerr cell containing water; the Kerr cell formed part of a high frequency generator which oscillated at from 3 to 10 meters wave-length depending on the capacity. The light, after passing through the cell was photographed with a quartz spectrograph. It was found that certain of the lines were displaced toward the red by .06A when the high frequency oscillator was operating. In the region examined in detail from 2480 to 2500A with a microphotometer, two lines showed the change in wave-length, the wave-length of the other 15 in this region being unchanged. The frequency shift was found to be independent of the amount of the oscillatory current in the circuit, and also independent of the temperature of the water in the range from 20° to 60°C which was investigated.

10. The recombination spectra of the halogens. H. C. UREY AND JOHN R. BATES, The Johns Hopkins University.—The emission spectra of flames of hydrogen and chlorine and of hydrogen and oxygen containing chlorine, bromine and iodine have been observed with the expectation of securing the continuous recombination spectrum when the following reactions take place: (a) $H+X \rightarrow HX$ or $H+X' \rightarrow HX$ and (b) $X+X' \rightarrow X_2$. The hydrogen chlorine flame emits a continuous spectrum extending to about 3200A with no evidence of structure. The flame containing H_2, O_2 and halogens emit the water bands, the continuous spectra and a faint near ultra-violet banded spectrum whose spacings varied with the halogen present. This band spectrum is believed to be due to some molecule of halogen and oxygen. The limits of the continuous spectrum for chlorine, bromine and iodine change to longer wave-lengths in the order given. The relative positions of the violet limits of these spectra can be qualitatively explained by the Franck-Condon theory applied to the reaction (b) above assuming that the temperatures of the flames are the same. These limits are such that they are emitted by two colliding atoms one in the $^2P_{3/2}$ and the other in the $^2P_{1/2}$ state having the sum of the relative kinetic energy and the energy of excitation of the one atom equal to about 14000 wave-numbers. Enough collisions of this class may be expected in the flames to account for the energy radiated. The possibility that the continuous spectrum is due wholly or in part to the reaction (a) cannot be excluded.

11. Directional distribution of the relative velocity of the decomposition products in the optical dissociation of sodium iodide. ALLAN C. G. MITCHELL, Bartol Research Foundation of the Franklin Institute.—Sodium iodide may be dissociated by ultra-violet light into an excited sodium and a normal iodine atom, the energy necessary corresponding to a wave-length of λ2450. When a wave-length shorter than λ2450 is used the excess energy goes into relative kinetic energy of the two atoms as they fly apart and the excited sodium atom emits *D*-lines with a corresponding Doppler broadening. The following experiment was designed to show whether the two atoms have any tendency to fly apart in the direction of the electric vector of the exciting light. A beam of light from a powerful Cd (λ2399–2144) or Zn(λ2139–2026) spark, respectively, was directed into a quartz tube containing NaI vapor. A photometer arrangement containing a sodium absorption cell served to measure the percentage absorption and hence the Doppler broadening of the *D*-lines. By making observations perpendicular and parallel to the beam of exciting light, the relative kinetic energy of the two atoms, and hence their tendency to fly apart in a given direction was measured. The percentage absorption of sodium light observed in either direction was the same. Hence, it was concluded that the atoms fly apart in either direction with equal probability.

12. The emission of positive ions from tungsten at high temperatures. LLOYD P. SMITH, Cornell University.—It has been found that a tungsten filament, after being flashed at a tem-

perature above 3000°K and operated at 2500°K for ten hours in order to remove impurities such as alkali metals, emits positive ions. The ion current is steady and is related to the temperature of the filament by the relation $-i_+ = AT^2 e^{-b/T}$. It's magnitude at 2500°K is about 6.6×10^{-8} amperes per square cm of emitting surface. The mass of the ions could not be determined by using the principle of the Hull magnetron with a collecting cylinder 3.2 cm in diameter and an axial magnetic field of 5000 gauss, under a difference of potential of 20 volts between the filament and cylinder. This shows that the mass of the ion is greater than that of a potassium ion. Theoretical considerations indicate that the ions are produced in the tungsten and may be tungsten ions. The ion current at a given temperature remains unchanged when an inactive gas such as argon is admitted to the tube provided its density does not become great enough to appreciably cool the filament.

13. Arcs with small cathode current density. J. SLEPIAN AND E. J. HAVERSTICK, Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.—A theory of the cathode of an arc based on the drawing of electrons from a thermionically inactive electrode by very intense electric fields has been proposed. This field is maintained by space charge of positive ions next to the cathode, and it may be shown that this requires a current density of more than 1000 amps/cm² even at low gas pressures. Experiments have been carried out demonstrating the existence of arcs with current densities of less than 100 amps/cm² so that the above theory seems untenable in the case of these arcs.

14. Striking potential of aluminum arc. S. HERBERT ANDERSON AND WILLIAM BLEAKNEY, University of Washington.—In a report made at the Los Angeles meeting, May 1927, it was pointed out that Simeon's theory of the striking potential of metallic arcs (Phil. Mag. **46**, 816, (1923)) was not substantiated. Further investigation with aluminum electrodes in atmospheres of hydrogen, nitrogen, oxygen and air indicates that: (1) a gaseous atmosphere is necessary for the striking of the arc; (2) the striking potential depends upon the nature of the surrounding gas and its pressure, as well as the nature of the electrodes.

15. Probe and radiation measurements in the normal copper arc. W. B. NOTTINGHAM, Bartol Research Foundation.—The Langmuir probe has been used to measure the electron temperature, the space potential, and the positive ion concentration in the stream of the copper arc. With an increase in the arc current from 2.5 to 6.0 amp., the electron temperature decreased from 19,000°K (2.45 volts) to 15,500°K (2.0 volts). The electrons gain energy from the field and make elastic collisions until they have sufficient energy to excite the atoms. Thus the average velocity is probably controlled by the electron transition in the copper atom from the metastable "D" level to the 2^2P level involving energies of 2.14 and 2.4 volts. For arc currents from 2.5 to 6.0 amp., the positive ion concentration increases according to the equation $n_+ = ae^{bI}$, where I = arc current and a and b are constants. The intensity of the resonance radiation λ3274 and λ3248 emanating from the arc stream half way between the electrodes is related to the current by $l = ce^{2bI}$ where l = light per unit volume. These equations give $l = (c/a^2)n_+^2$. Since the electron and the positive ion concentrations are equal in the arc stream, this relationship shows that the major part of this radiation is due to some cumulative action.

16. The time lags of spark gaps in air at various pressures. J. W. BEAMS AND J. C. STREET. University of Virginia.—Using a method described by one of us (Beams, Jour. Franklin Institute: in press) the time between the application of the over-voltage and the spark discharge, that is, the so called "time lag" of the spark in air at various pressures has been measured. This time lag was found not to be a definite magnitude but to vary with the number and distribution of the ions in the gap at the time of application of the voltage. When ions were blown into the gap or generated there by radioactive material the lags were shortened. On the other hand, when the air was dry and free from ions, the lags were very much lengthened. If the pressure is raised or the voltage applied to the gap lowered, the lags were increased. The fields used always exceeded 50,000 volts per cm at some point in the gap and were applied by as steep wave fronts as could be obtained. Under certain conditions in moist air at atmospheric pressure the lags could be made as short as 10^{-8} sec.

17. The distribution of ionic mobilities in moist air. JOHN ZELENY, Yale University.—The preliminary work previously reported (Phys. Rev. **31**, 1114, (1928)) has been completed for air having a water content between 1.5 mg and 7.6 mg per liter. A modified procedure permits an evaluation of the effects of diffusion and mutual repulsion of the ions. When corrected the results still show a band of distribution of mobilities which for the positive ions extends about 40 percent and for the negative ions about 30 percent of the lowest value. The corrected mobilities for the centers of the bands, at atmospheric pressure and at 20°C, for the negative ions and the positive ions respectively are $2.00 \pm .02$ cm/sec. · volt/cm and $1.22 \pm .02$cm/sec. · volt/cm.

18. Shot effect of secondary electrons. LUCY J. HAYNER AND A. W. HULL, General Electric Company.—The shot-effect of secondary electrons from plates of triode tubes was measured with a tune-circuit amplifier at 10^6 cycles, introducing calibrating voltages into the tuned input circuit. Calculations of the electronic charge from shot-effects of temperature-limited primary currents, to check the method, agreed within 1 percent with Millikan's value. Measurements were made on five tubes having different secondary emissivities. The average number of secondaries per primary electron, ω, ranged from 1 to 4.5. In every case the shot-effects of both grid and plate currents were measured and found greater than those of equal primary currents. This was expected since there are random fluctuations of ω superposed on the fluctuations of the primary current. For large ω, shot-effects several times larger than those of equal primary currents were observed, due to the fluctuations of ω. Applying Campbell's general expressions for shot-effects of secondary emission, it is concluded from the observed differences between the plate and grid shot-effects that secondary emission is simultaneous with primary impact within 10^{-8} sec. Since results of Hull and Williams indicate at least partial independence of these two events at 10^6 cycles, this investigation will be extended to higher frequencies.

19. Maximum excursion of the photoelectric long wave limit of the alkali metals. HERBERT E. IVES AND A. R. OLPIN, Bell Telephone Laboratories, Inc.—Earlier experiments have shown that the long wave limit of photoelectric action in the case of thin films of the alkali metals varies with the thickness of the film. A maximum value is attained greater than that for the metal in bulk, which for the majority of the alkali metals lies in the infra-red. The wave-length of the maximum excursion of the long wave-limit has been studied for Na, K, Rb and Cs. *In each case it is found to coincide with the first line of the principal series, i.e. the resonance potential.* It is suggested that photoelectric emission is caused when sufficient energy is given to the atom, to produce its first stage of excitation. The identity of photoelectric and thermionic work functions suggests that atomic excitation is the initial process in thermionic emission as well.

20. A photo-e.m.f. in single crystals of selenium. R. M. HOLMES AND N. L. WALBRIDGE, University of Vermont.—The photo-e.m.f. reported (Phys. Rev. **31**, 1126, (1928)) for acicular crystals is now found in greater magnitude with thin lamellar single crystals. A translucent platinum film is sputtered on each of the two parallel faces of the crystal. The films are connected to a galvanometer. When the radiation from a tungsten lamp, using a water cell, passes through one film, electrons flow from selenium to platinum at the illuminated contact. By simultaneous illumination of both sides or by the introduction into the galvanometer circuit of an opposing p.d. this photo-current may be reduced to zero. The relation between this balancing p.d. and light intensity and the relation between photo-current and light intensity have been investigated. The balancing p.d. increases rapidly with illumination and finally reaches a nearly constant value sometimes as high as 130 millivolts for 0.4 lumen/cm^2. The photo-current continues to increase with illumination, becoming as high as 5.5 microamperes for 4 lumens/cm^2. Preliminary investigation with an equal energy spectrum shows a maximum with green and a slight reversal with red light. A decrease in the photoelectric work function by altered image attractions may explain the photo-e.m.f. and current. The effect is not thermoelectric.

21. Fatigue in the cathodo-luminescence of zirconia. D. T. WILBER, Cornell University.—The luminescence of zirconia, produced by the discharge from a cold cathode was found to reach a maximum and decrease sharply while the vacuum, voltage and current in the tube increased together. (Phys. Rev., **17**, 713, (1921)). By using a hot cathode and varying the vacuum, voltage and current independently, it is found that the maximum does not depend on vacuum but upon the power delivered on the zirconia and the consequent heating as measured by a thermo-couple. The previously observed maximum may also be associated with the decrease in thermal conductivity of air at low pressures. All bright luminescence results in a temporary decrease in luminescent power due to heating and a permanent fatigue due to reduction and blackening of the oxide. Standing in air restores the luminescence lost by deoxidation. A brief luminescence of extreme brilliancy is obtained from a thin coating of zirconia on a copper rod which is cooled by liquid air, when the zirconia is bombarded with 30 m.a. at over 10 kv. This intense luminescence is scarcely less brilliant than the incandescence which follows it at once.

22. Persistence of λ2537 in mercury at low pressures. HELEN A. MESSENGER AND HAROLD W. WEBB, Columbia University.—The persistence of λ2537 was measured for mercury vapor pressures corresponding to the temperature range 78° to −19°C. The radiation was excited by electron impact and detected by a nickel photoelectric plate in a modified Lenard tube. A quartz window prevented metastable atoms from reaching the plate. The alternating potential method previously described (Phys. Rev. **21**, 479, (1923)) was used to measure the persistence. The persistence expressed as the time constant of a simple exponential decay varied from 4×10^{-4} sec. at 78° to 10^{-7} sec. at −19°C. In the temperature range between 78° and 17° the time constant varied as the first power of the pressure and not as the square of the pressure as predicted by the simple theory of diffusion of radiation. The values of the time constant were, however, so small that it still seems necessary to explain the persistence as due to a series of absorptions and reemissions, with possibly a wave-length change at each step. The life of λ1849 was found to be less than 3×10^{-9} seconds. Two other radiation processes were observed, one having a life of 2×10^{-6} seconds, excited at 7.1 volts, and the other a life of about 8×10^{-5} seconds, excited between 5 and 6 volts.

23. Sound radiation from a system of vibrating circular diaphragms. IRVING WOLFF AND LOUIS MALTER, Radio Corp. of America.—Using the expression for the velocity potential due to a point source radiating into a semi-infinite medium Lord Rayleigh has determined the sound radiation from a vibrating circular diaphragm in an infinite wall. Following the same method, the radiation due to any shaped diaphragm or combinations of diaphragms can be determined. Curves are given for circular diaphragms showing the distribution of pressure over the surface bounding the semi-infinite medium. These curves enable the determination of the radiation from any combination of vibrating circular diaphragms placed in the surface. Calculations have been carried out for a number of special cases. At low frequencies the diaphragms react upon each other to increase the efficiency of radiation. This effect vanishes at high frequencies. The mutual aid of the diaphragms decreases very rapidly as the distance between the diaphragms is decreased. In certain cases the combination may result in decreased efficiency over particular frequency ranges. These results are all explainable on the basis of phase differences between the motion of a diaphragm and the pressure over the surface of another diaphragm due to the motion of the first.

24. Sound propagation. D. G. BOURGIN, Department of Mathematics, University of Illinois.—A theory of the propagation of sound has been developed based on the balancing of internal and kinetic energies by collisions of the first and second kinds. Radiation effects are included without change in the formulas but it appears that, except for high temperatures or low densities their rôle is negligible. The asymptotic expansions at high frequencies contain only parameters involved in the long wave-length formulas. The extension of the theory to gas mixtures marks, it is believed, the first attempt to treat sound kinetics in mixtures. The low frequency velocity is given by the quotient of a cubic by a bi-quadratic and the absorption term by the ratio of a bi-quadratic to a septic polynomial in the concentrations. The formu-

las simplify when it may be assumed that, approximately, the effect of foreign molecules in promoting transfers is the same as that of molecules of the same gas (cf. a preliminary abstract in Nature). Only if, besides this, the gases have the same number of degrees of freedom and comparable molecular weights does the theory support Abello's interesting empirical suggestion of linearity of dependence of the difference in absorption coefficients on concentration.

25. Conditions for securing ideal acoustics in auditoriums. F. R. WATSON, University of Illinois.—A study of recent investigations in auditorium acoustics indicates (Acoustics of Auditoriums, Science, March 30, 1928. Ideal Auditorium Acoustics, Journ. Am. Inst. Architects, July 1, 1928.) that ideal acoustics can be obtained by two procedures. First, to surround the speaker or musician with suitably arranged reflecting surfaces so that he can "hear himself" and then adjust his performance to secure the best generation of sound; and second, to adjust the auditorium so as to approximate the reverberation conditions of an outdoor theater, which is generally regarded as "perfect" for hearing. Reflected sounds reaching the auditors within 0.05 second after the direct sound are beneficial in reenforcing words, (Petzold, Elementare Raum Akustik.) but sounds coming later than 0.05 second produce a blurring and should be absorbed at the reflecting surface. It can be shown that reflected sound is not as important in securing loudness as heretofore supposed. Experimental evidence supports the preceding theory and points the way for securing ideal acoustics.

26. Comets and terrestrial magnetic storms. H. B. MARIS AND E. O. HULBURT, Naval Research Laboratory.—Practically all observed details of terrestrial magnetic storms have recently been shown to be explainable by the assumption that the solar disturbance is a half-hour ultra-violet flash, such as would come from a spot at 30000°K and 1/10000 of the solar disk in size. Such a flash would be expected to cause changes in comets much as it does in our own atmosphere, and we find that this is so. For, in nearly every instance the date on which a comet was observed to undergo an unusual change, such as breaking up of the nucleus, loss of tail, sudden increase in brightness, etc., was found to follow within a week the date on which a strong magnetic storm occurred on the earth, provided the necessary condition was fulfilled that the earth and the comet were approximately on the same side of the sun. When the comet and the earth were on opposite sides of the sun, changes in the comet were found to occur between periods of terrestrial magnetic storms separated by a solar rotation. Further, the action of the ultra-violet light of the quiet (undisturbed) sun on the nucleus is shown to account for some hitherto unexplained characteristics of the tail.

27. Weather forecasting by the intensity of radio signals. R. C. COLWELL, West Virginia University.—Observations made at Morgantown, West Virginia upon the signal intensity of station KDKA at Pittsburgh, Pa. have shown that the intensity of the signal after sunset is very variable. The variations are shown graphically upon the paper strips of a Shaw Recorder. Curves taken at various times over a period of two years indicate that increasing intensity after nightfall foreshadows cloudiness or rain for the following day; while decreasing intensity is a sign of clearing weather the next day. The results obtained from the fading curves are compared with the usual prognostications for several weeks of the past autumn.

28. The sun's radial magnetic gradient and atmosphere. ROSS GUNN, Naval Research Laboratory.—*Theory of the rapid radial magnetic gradient of the sun based on diamagnetic effect of ions in the reversing layer.* A theory of the sun's radial magnetic gradient has been worked out which explains quantitatively the phenomena in terms of the diamagnetic effect produced by ions spiralling about the impressed magnetic field. The free paths, temperature, ionization and magnetic field are precisely those most effective in producing a large diamagnetic effect. This diamagnetism explains adequately the extraordinarily large observed gradient and an extrapolation of the effect into the lower layers where the diamagnetic effect drops to low values indicates that the polar field strength at the surface of the sun may be several times the present accepted value. *Ionic densities have been obtained as a function of the altitude above the photosphere.* The ionic densities derived from the diamagnetic relations agree with densities inferred from other unrelated sources. The effective atomic mean weight of the particles in the sun's atmosphere is found to be approximately 3.3.

29. Resistance of bismuth in alternating magnetic fields. WILLIAM W. MACALPINE, Columbia University.—An oscillator was constructed with a 50 watt tube producing fields up to 50 gauss r.m.s. at 10^6 cycles in a coil 3/4" diameter by 2" long to modulate a constant field. Bismuth wire was wound bifilarly on a bakelite tube placed inside the solenoid and both immersed in liquid air. A single turn of copper wire around the tube served to measure the field strength and phase. Direct current was passed through the bismuth wire, and being held constant by a radio frequency choke, an alternating voltage appeared across its terminals proportional to and in phase with its resistance. To measure this voltage in phase and magnitude a double potentiometer was constructed. The change in resistance of the bismuth wire was found to be in phase with the field and equal in magnitude to that which was calculated from d.c. measurements of resistance against field strength. The overall precision was about 5 percent. Similar work had been done at 50,000 cycles and room temperature when the effect was also found to be normal. Fields up to 700 gauss r.m.s. between dust core poles were obtained at the latter frequency.

30. The specific resistance of beryllium. EVAN J. LEWIS, Cornell University.—A rod of metal obtained from the Beryllium Company of America was used to determine the specific resistance of Beryllium from the temperature of liquid air to 700°C. The experiment was performed by the "fall of potential" method. At first a decided lowering of the resistance was observed while the temperature remained constant or nearly so. After a prolonged heat treatment, however, the resistance of the speciman reached a final, steady state and results were reproduced in successive trials. The value found was about 6.8 microhm-centimeters at 20°C.

31. Double-valued characteristics of a resistance-coupled feed-back amplifying circuit. PRESTON B. CARWILE, Lehigh University.—A Hartley resistance-coupled feed-back amplifying circuit may be connected in such a way that under ideal conditions the feed-back control does not affect the non-feed-back amplification factor. The total amplification is then a simple function of two independent variables. When the feed-back action goes beyond a certain critical value two non-reversible discontinuities appear in the characteristic curve between output and input voltage. Between these points of discontinuity the characteristic has two branches, representing two possible values of output voltage for each single input value. A simple explanation accounts for the two discontinuities, their non-reversibility, and the double valued characteristic.

32. High amplification by making use of grid currents. PETER J. MULDER AND JOSEPH RAZEK, University of Pennsylvania.—The mutual conductance of a vacuum tube was found apparently to change on the insertion of a high resistance into the grid circuit. With a well insulated grid, the apparent change varied in a definite manner with the value of the grid resistance inserted. Assuming $E_g = E_c - Ri_g = E_c - Rki_p$; $\partial i_p/\partial E_c = G' = G/(1+RkG)$ where G is the mutual conductance, R is the external grid resistance, k is the ratio of the grid current to the plate current, and E_c is the biasing voltage. For a 312A tube, with negative grid potentials of 2.5 volts or more, k is negative and constant. When operating in this range, and using a suitable value of R, the apparent value of G can be made very large. For amplification of photoelectric or other small currents, we obtain $\partial i_p/\partial i_s = GR/[(1+JR_1)(1+R/r)+RkG$ where i_s is the photoelectric current, r is the grid-to-ground resistance, J is the plate conductance, and R_1 is the external plate resistance. Using a photoelectric cell connected to the grid of a 312A tube, and giving to this grid a negative bias through a suitable resistance, we have obtained an amplification of 16 million. The photoelectric current was measured on a sensitive galvanometer (2×10^{-11} amp/mm) and the corresponding tube plate current change was measured on a milliammeter.

33. Photoelectric spectro-photometer. JOSEPH RAZEK AND PETER J. MULDER. University of Pennsylvania.—A photoelectric spectro-photometer consisting of an optical system, a photoelectric cell, and vacuum tube amplifier has been built. The amplifier comprised two vacuum tubes placed into the arms of a bridge. The sensitivity of this circuit was found to be

$\partial I_G/\partial E_g = G/[2+R_G(J+1/R_1)]$ where J and G are respectively, the plate, and the mutual conductance of the tubes, R_1 is the external plate resistance, and R_G is the galvanometer resistance. It was subsequently found that the same circuit has already been described by Wynn-Williams (Proc. Cam. Phil. Soc. **23**, 810, (1927)) who gives a similar sensitivity expression. We have obtained a sensitivity of 500,000 mm/volt with good stability. The addition of grid resistors of proper magnitude will increase the sensitivity. The computed and measured values of the amplification agree to 1 percent, which is the accuracy to which the quantities involved were measured. The light to be examined is passed through a spectrometer into the photoelectric cell. The cell is connected to one grid in the bridge circuit. The deflection of the galvanometer is a function of the light intensity. Spectral curves of light from an arc and of light diffusely reflected from opaque objects were obtained. A portable self-recording instrument embodying these ideas is in course of construction. It is believed that this device will prove simpler than others recently suggested for the same purpose.

34. Perturbations in band spectra. JENNY E. ROSENTHAL AND F. A. JENKINS, New York University.—Curves for the deviations of the lines at the perturbations in the states $n'=12$ and $n''=11$ of the violet CN system have been completed. They show additional examples of the resonance form previously reported. (Phys. Rev. **31**, 539 (1928)). The wave mechanics treatment of perturbations given by Kronig (Zeits. f. Physik **50**, 347(1928)) interprets them as due to the coincidence of terms of equal j in two different electronic states. The level $n=11$ in the lower ^2S state of the violet CN bands lies close to that of $n=4$ in the ^2P initial state of the red bands. An investigation of the structure of the (4, 2) band of the latter system (from a plate kindly furnished by Roots and Mulliken) shows a perturbation similar to the above in the $^2P_{3/2}\rightarrow{}^2S$ sub-band. As expected, its maximum occurs at the same rotational quantum number ($j=13$) as that for the corresponding perturbation in the ^2S state. Other features in agreement with the theory are (1) the deviation of the terms are in the opposite sense from those in the ^2S perturbation, (2) only one of the components (symmetric or anti-symmetric) of the σ-doublets is affected. The $^2P_{1/2}$ levels of $n=4$ are also perturbed at a higher value of j.

35. Detection of the Isotopes of lead by means of their oxide band spectra. SIDNEY BLOOMENTHAL (Introduced by R. S. Mulliken) University of Chicago.—The band spectra from an ordinary lead arc and from one containing lead of atomic weight 206 (uranium lead) have been photographed in the second order of a 21-ft. Rowland grating. A similar comparison has been made by Grebe and Konen (Phys. Zeit. **22**, 546(1921)) who found that the band lines from uranium lead near 4250A were sharper than those of ordinary lead, and displaced 0.055A towards shorter wave-lengths. The differences noted here agree with those predicted by the theory of the isotope effect in band spectra with PbO as the emitter if ordinary lead contains as principal istopes atomic weights 208, 206, 207 with the relative abundance in this order. For instance each strong line near the head of the λ5678.5 band obtained from Pb206 corresponds to the long wave component of a group of three equally spaced lines in the spectrum of ordinary lead the weak central member (Pb207) of which is separated from the two outer components (Pb208 and Pb206) by 0.125A. These results agree with Aston's positive-ray analysis of ordinary lead.

36. Formation of MH molecules; effects of H atom on M atom. ROBERT S. MULLIKEN, University of Chicago.—Observed electronic states of diatomic hydride molecules (CH, NH, OH, MgH, CaH, ZnH, CdH, HgH, etc.) are derivable from unexcited H plus familiar low-energy states of M atoms (Hund, Hulthén, Mecke, Mulliken). Observed states and especially observed $\Delta\nu$ intervals in ^2P or ^3P states of such MH molecules indicate that the effects of the H on the M atom are confined essentially to the following; (1) the couplings (if any) between l_τ vectors of M atom outer electrons to give a resultant l are completely broken down by the field of the H nucleus; the M atom orbits are otherwise scarcely changed, except for slight shielding or similar effects produced by the H electron and nucleus; the usual l_τ selection rules are, however, abolished; (2) the uncoupled vectors l_τ are separately space-quantized with reference to the electric axis, giving component quantum numbers σ_{l_τ}; (3) the electron of the H atom ($\sigma_{l_\tau}=0$) takes its place with the M electrons, sometimes becoming equivalent to one

of them giving a new closed shell (of two electrons); (4) the original couplings of s_r vectors are often broken down; always, the spin of the H electron alters the original multiplicity by one unit.

37. Computation of properties of certain excited states of H_2. E. C. KEMBLE AND C. ZENER, Harvard University.—A first order perturbation theory computation of the potential energy curves for the two-quantum *P*-type states of interacting pairs of H atoms (Cf. E. C. Kemble, Phys. Rev. **31**, 1131, (1928)) shows that two of these states have the potential energy minima requisite for molecular formation. One is a singlet state to be identified with the upper energy level of the Werner bands while the other is a triplet state which may be identified with the 2^3P state reported by Richardson (Proc. Roy. Soc. A, **114**, 643, (1927)). The agreement of the computed curves and the empirical data is fair. The theoretical confirmation of the existence of a 2^3P state shows that London's valence theory needs modification when applied to the excited states of symmetric diatomic molecules where the wave functions are multiply degenerate at infinite internuclear distances. A similar calculation for the remaining (*S*-type) two-quantum states of the H_2 molecule is in progress.

38. The spectra of trebly ionized vanadium, V IV and quadruply ionized chromium, Cr V. H. E. WHITE, Cornell University.—The neutral atoms of vanadium and chromium contain five valence electrons, $3d^3\,4s^2$, and six valence electrons $3d^5\,4s$, respectively. The removal of three electrons $3d\,4s^2$ from vanadium and four electrons $3d^3\,4s$ from chromium yields two isoelectronic systems, V IV and Cr V, the lowest energy levels of which are represented by the two remaining electrons $3d^2$. The spectra from these two systems should resemble very closely the spectra of neutral calcium, singly ionized scandium and doubly ionized titanium. Extrapolations from the already known data of Ca I, Sc II, and Ti III, to V IV and Cr V have led to the identification of some thirty energy levels in both triply ionized vanadium and quadruply ionized chromium. The strongest lines in these spectra arise from combinations between ^3P, $^3D'$, ^3F, ^1P, $^1D'$, ^1F $(3d4p)$ and ^3D, ^1D $(3d4s)$, and ^1S, $^3P'$, ^1D, $^3F'$, ^1G $(3d)^2$. The latter configuration gives the lowest levels in the spectrum. The Moseley diagram and the irregular doublet law served admirably in determining the approximate positions of the various singlet and triplet levels as well as the approximate location in the spectrum of the radiated frequencies. The ionization potentials, that is the voltage necessary to remove one $3d$ electron from the normal state $^3F_2$ $(3d)^2$ of V IV and Cr V, to the normal state $^2D_2$ $(3d)$ of the once more ionized atoms are determined at about 48.2 volts and 72.4 volts respectively.

39. The hyper-fine structure of singly ionized praseodymium. R. C. GIBBS AND H. E. WHITE, Cornell University.—Recently King at the Mt. Wilson Observatory in photographing the furnace, the arc, and the spark spectra of the rare earth group of elements found that a great many of the praseodymium spark lines, Pr II, show what may be called hyper-fine structure. Using the large solar spectrograph on Mt. Wilson, dispersion 1.5A per centimeter, one of the authors photographed some of the more prominent hyper-fine groups within the region 3900–5000 Angstroms. All of the completely resolved hyper-fine structures reveal six components. The frequency intervals between the hyper-fine structure for any one set of six lines follow very closely the Landé interval rule and the relative intensities of the lines in each group decrease with the interval. Some of these groups of lines show decreasing intervals and intensities toward longer wave-lengths while others are similarly degraded toward shorter wave-lengths. For example, one group at about λ4756 degrades toward the violet with outside components separated by 0.33A, while another group at about λ4747 degrades toward the red with outer components separated by 0.22A. A theoretical interpretation requires the introduction of quantum conditions in addition to those necessary for ordinary line spectra. At present it is suggested that the new quantum conditions may be associated with either a spinning nucleus or with a $4f$ electron. Before attempting to interpret these observations further, Zeeman patterns of these hyper-fine structures will be studied.

40. An exception of Pauli's g-sum rule. J. B. GREEN, Ohio State University, and R. A. LORING, Northwestern University.—According to Pauli's *g*-sum rule, the sum of the splitting-

factors of all terms of the same inner quantum number of any configuration of electrons, is the same as the sum gotten from the use of the Landé g-formula, even though the single value for the different terms are not those calculated from the formula. This rule has been found valid in most spectra investigated, well within the limits of experimental error. In the lowest configuration of Sb, s^2p^3, Hund's theory gives $^4S_{\frac{3}{2}}$, $^2D_{2\frac{1}{2}}$, $^2P_{1\frac{1}{2}}$, as the possible levels. Of these, $^2P_1$, is the only one with inner quantum number $\frac{1}{2}$, and should, therefore, according to the above rule, have the theoretical g-value, namely. The line selected to test this is the combination $^2P_1{}^2P_2$, 3029.824. The line gave a Zeeman pattern, $\overline{(0.268)}$ 1.019 $\overline{1.544}$, as a mean of three sets of plates taken with the Paschen-Runge mounting at the Jefferson Physical Laboratory. The plates were measured in the second and third orders, dispersions of 0.97 and 0.65A/ mm respectively and checked by microphotometer measurements. The g-values determined from the measurements are 0.740 and 1.276, while the value 1.285 was found for one of the terms from independent measurements on another line. The theoretical value for $^2P_1$ is 0.667. This leaves a discrepancy of over 11 percent to be accounted for. The experimental error was certainly under 3 percent.

41. The use of series inductance in vacuum spark spectra. ALICE M. VIEWEG, C. W. GARTLEIN AND R. C. GIBBS, Cornell University.—In attempting to extend the identification of lines in the Cd I sequence as partially reported by us for Sb IV and Te V at the Pomona meeting last June, it became necessary to have another criterion, in addition to the ordinary methods of identification, in order to distinguish the lines emitted by an atom in its various stages of ionization. Some lines that satisfied many criteria had been already reported as belonging to other stages of ionization. Somewhat as in the case of ordinary sparks in air inductance in series with a vacuum spark, utilized to some extent by Fowler, has served to strengthen lines arising from lower states of ionization and to weaken lines coming from atoms that are highly ionized. By making several exposures on the same plate, it has been possible in some cases to sort out, from the relative quality of the lines, radiation coming from five different stages of ionization. While some detail is lost by reproduction and enlargement many of these differences are readily recognized in a lantern slide projection. Thus it nas been found possible by these added criteria to identify lines belonging to the various multiplets with much greater certainty.

42. Regularity in frequency shifts of scattered light. W. F. MEGGERS AND R. M. LANGER National Research Fellow, Bureau of Standards.—Published data on combination scattering seem to show a capriciousness as to which lines of the source are capable of exciting the modified lines, and as to which modified lines a particular line of the source will excite. There are also much greater variations in frequency shift than the precision of measurement estimated. These irregularities are not real. For example, in benzol, in the spectral region used (3000–6600A) all the stronger lines namely 3126, 3132, 3341, 3650, 3654, 3663, 4047, and 4358 give rise to all the stronger shifted lines (i.e., shifts of 606, 848, 992, 1178, 1584, 3059 wave numbers). In some cases the shifted line falls on an Hg line and is not observed. There are about 50 lines observed in this region. In CCl_4 and $CHCl_3$ there are even more. Shorter wave-lengths are not useful because of absorptional chemical action. The relative intensity and character of different modified lines due to a given exciting line are about the same no matter which exciting line is taken. The relative intensity of a given frequency shift usually increases slowly as the exciting frequency increases. More accurate measurements of frequency shifts (using 21-ft. grating) show them to be independent of the exciting line within one wave number. This work will be published in the Bureau of Standards Journal of Research.

43. Mercury spectrum by high voltage electrodeless discharge. OTTO STUHLMAN, JR. AND M. W. TRAWICK, University of North Carolina.—Spectra of the electrodeless discharge through a capillary and of the ring discharge in a 12 cm spherical bulb were compared with the spectrum from a quartz mercury vapour lamp. Spectrograms of the ring and capillary discharge were made at 25°C and 5 microns pressure; frequency of damped oscillations 1.5×10^8; capacity .0016 mf; sparking voltage 18×10^3; intensity controlled by spark gap. The spectrum of the discharge through a capillary is identical with that of the luminous ring discharge in the bulb.

Spark and arc lines are about equal in number. No continuous spectra were observed under above conditions. In $1s-mp_1$ frequencies up to $m=17$ were classified. Twelve faint lines beyond this frequency are as yet unclassified.

44. Excitation of sodium by ionized mercury. HAROLD W. WEBB AND S. C. WANG, Columbia University.—Rayleigh has shown that metallic vapors are excited by ionized vapors distilled from arcs of other vapors. (Proc. Roy. Soc. A **112**, 14, (1926)). We have studied the excitation of sodium by mercury vapor distilling from an arc, mixing the vapors at a great distance from the main arc to avoid direct excitation by electrons. By an auxiliary electrode directly excited 2^3P mercury atoms were introduced into the stream of ionized mercury vapor, in order to differentiate between the effects due to excited atoms and those due to ions. The excitation by ions may be explained as due in part to the ionization of the sodium but also in large part to the production of excited mercury atoms by the recombination of mercury ions and the subsequent excitation of the sodium. There is, however, strong evidence that the process involves a three-body impact between a mercury ion, a normal sodium atom and an electron. This is suggested by the nature of the sodium spectrum and by the marked enhancement of the mercury lines originating at the 3^3S and 3^1S levels produced by the introduction of sodium vapor into the ionized mercury. There was no indication of direct electron excitation in this apparatus, although Rayleigh's results indicate that this type of excitation may have been important in his apparatus.

45. The Weiss, Planck and Rydberg constants in the theory of the electromagnetic quantum. CORNELIO L. SAGUI, Castelnuovo, Dei Sabbioni, Arezzo, Italy.—To a neutral proton an electron is added. Its electromagnetic undulatory energy would flow into the proton as a circular current directed downward, of which the work on a unitary pole would be $2r\times1.6\times10^{-20}$. The energy corresponding to this work would be distributed among the 60 levels of the proton; therefore $\mu=2r\times1.6\times10^{-20}/60=1.7\times10^{-21}$, Gauss·Cm is its value appearing at the surface level of the proton as a magnetic mòment, the Weiss constant. A radiation must be referred now to $\frac{1}{2}\mu^{1/3}$ since μ is the volumetric energy distributed on both sides of a level, and an oscillating electron would have only one degree of freedom along one dimension only of the euclidean space. It was found that the voltage $V=r\mu^{1/3}$ for one oscillation only. It was also found that $e(r\mu^{1/3})=h=1.6\times10^{-20}\times3.14(1.85\times10^{-21})^{1/3}=6.18\times10^{-22}$, the Planck constant. Since the proton is supposed to be made up of 1830 electrons distributed among 60 levels, each electron in each level contributes the energy h and the whole energy of a proton would then be $60\times1830\ h=109800h$, where 109800 is the Rydberg constant in waves/cm. The results check each other fairly well.

46. Radiation and the electron. R. D. KLEEMAN, Schenectady, New York.—The author in his investigations on the zero of internal energy and entropy was led to deduce thermodynamically that the electron possesses the following properties:—1. It may possess internal energy apart from kinetic energy. 2. The whole, or a part, of its internal energy may be converted into electromagnetic radiation, apart from emitting radiation on undergoing acceleration. 3. It may absorb radiation in indefinite amounts and convert in part into internal energy. 4. If in motion, the absorption of temperature radiation tends to decrease its kinetic energy and increase its internal energy, in a degree depending on its internal energy. 5. The electric force acting upon it when in a field depends on its internal energy. An alternate proof of these properties may be obtained by making use, besides, of some of the fundamental notions in kinetic theory and electromagnetic radiation. By means of the foregoing properties and the principles of conservation of momentum and kinetic energy, and making use of the fact that radiation takes place in quanta, the various phenomena involving the interaction of radiation and the electron may readily be explained.

47. Proposed interpretation of the fundamental quantum law. BENJAMIN LIEBOWITZ, 415 Fort Washington Ave., New York City.—If we regard $V=h\nu/e$ as an empirical relation between *voltage* and frequency *without reference to quanta*, suggestive interpretations present themselves. (1) The idea of a frequency proportional to a difference of potential, or energy,

or frequency follows immediately. (2) The fact that the voltage is propagated without change implies the concept of "wave-voltage" and suggests a close analogy to waves on wires. (3) From this view-point a light wave may be regarded roughly as consisting of a "core" of approximately longitudinal electric components surrounded by substantially transverse electric and magnetic fields analogous to the forces in and around a current-carrying filament. An expression for the maximum longitudinal force is derived: $E_s = 2\pi h\nu^2/ec$. Assuming this force to act on a free electron, values are obtained for the wave-length and amplitude of the resulting scattered radiation by means of both ordinary and relativity mechanics. The shifts exceed Compton's value 0.0243A by 5 percent at 1A and 37 percent at 0.2A. As developed thus far the theory gives only the *maximum* shift and indicates that the modified line should have a sharp long wave-length limit analogous to the maximum velocity limit of photoelectrons. The $(1-\cos\theta)$ law for a single electron follows as a simple Doppler effect.

48. A wave mechanism of quantum phenomena. R. V. L. HARTLEY, Bell Telephone Laboratories, Inc.—An analysis of the motions of a coupled mechanical system which differs from those ordinarily treated in that the coupling is a function of the magnitudes of the motions has led to the prediction of the appearance under certain conditions of subsynchronous motions in response to a simple single frequency driving force. The appearance of these additional frequencies has been verified by experiment. It is apparent that here is a process expressible in terms of ordinary materials and ordinary mathematics which allows quantum distributions of energy to arise, through simple mechanical restraints, from a continuous supply of vibrant energy. The analogy to the Raman effect is obvious. A consideration of the interrelations of matter and radiation has shown that the required conditions for the appearance of this effect can be satisfied by an atomic model based on a universal spacial distribution of charge of one sign. This charge obeys the laws of an elastic solid, and hence the relation between electric "pressure" and volume which serves as a coupling between longitudinal and transverse waves is non-linear. With this concept in mind a mechanical model of the universe may be imagined which will operate in remarkable accord with many observed phenomena.

49. Sigma-type doubling in the asymmetrical top. S. C. WANG, National Research Fellow, University of Wisconsin.—An elaboration and a more complete analysis of Witmer's work on the asymmetrical top (Proc. Nat. Acad. **13**, 60 (1927)) treated as a perturbation of the symmetrical one show that the complete Hamiltonian is diagonal in j and independent of m. Since there are $2j+1$ values of n for given j, the problem is equivalent to the reduction of a quadratic form in $2j+1$ variables to its principal axes. Without actually solving the characteristic determinant, we find the terms divisible into symmetric and antisymmetric groups just as in the sigma-type doubling in diatomic molecules treated by Kronig (Zeits. Physik. **50**, 347 (1928)), Hill, VanVleck and Mulliken (Phys. Rev. **32**, 250, 327 (1928)). Our doublet separation is, in Witmer's notation $\Delta\nu = [hcb^n(j+n)!]/[2^{3n}\pi^2(j-n)!^2]$ where $c = A^{-1} - (B^{-1}+C^{-1})/2$ and $b = (B^{-1}-C^{-1})/2c$. The formula obtained for the energy values agrees with Witmer's except for the inclusion of the doubling phenomenon. The experimental detection of this doubling, which is proportional to some power of b, would furnish a measure of molecular dissymmetry.

50. The classical theory of the Raman effect. E. H. KENNARD, Cornell University.—The Raman effect was predicted by Kramers and Heisenberg via the correspondence principle, but their treatment, being general, is very abstract. It may be of interest to describe a simple concrete example of the effect in classical theory. Consider the scattering of light by an electron in one atom of a polar diatomic molecule. For purposes of visualization a treatment by successive approximations is convenient. The force $eE \sin 2\pi\nu t$ due to the incident electric field of amplitude E would produce, in the absence of the other atom, a displacement $x = \gamma_\nu eE \sin 2\pi\nu t$ (e = electronic charge, γ_ν = a constant). This will alter the differential or polarizing force F_m on the electron due to the other atom by $\delta F_m = x\partial F_m/\partial x$, in which, F_m being dependent chiefly upon the distance s between the atoms, and the interatomic vibration of frequency ν_m being not quite harmonic, we can write $\partial F_m/\partial x = \sum_{r=1}^{\infty} a_r \sin 2\pi r\nu_m t$. Thus δF_m produces an additional displacement of the electron equal to $\delta x = \gamma_\nu \delta F_m = \gamma_\nu eE \sin 2\pi\nu t \sum_{r=1}^{\infty} \gamma_r a_r \sin 2\pi r\nu_m t$

$=\frac{1}{2}\gamma_r eE\sum\gamma_r a_r[\cos 2\pi(\nu-r\nu_m)t-\cos 2\pi(\nu+r\nu_m)t]$. There is no other term in the displacement of the first order in E. The term x causes the Tyndall scattering; the term, δx, scatters light whose frequencies are different from the incident frequency and are obviously related to the infra-red vibrational frequencies $r\nu_m$ in the manner characteristic of the Raman effect.

51. Collisions and coalescence of light quanta. A. L. HUGHES AND G. E. M. JAUNCEY, Washington University.—In view of several discussions (e.g. de Broglie, Witmer, and Rosenfeld) in which the possibility of collisions between light quanta, whether in a hohlraum or not, is contemplated, it is desirable to investigate what types of collision satisfy simultaneously (1) the conservation of energy, (2) the conservation of momentum, and (3) a microscopic reversibility in which both the forward and reverse processes are equally natural. It is found that the coalescence, on collision, of two quanta, whatever be the angle between their paths, cannot satisfy both conservation principles, nor is (3) possible unless one is prepared to postulate a spontaneous dissociation of a single quantum. Two quanta, however, can collide and give rise to two quanta with new frequencies and still satisfy all three principles. As a particular case, two quanta of the same frequency ν, in a 90° collision, give rise to one quantum of frequency 1.707ν, travelling forward along the line bisecting the 90° angle and a second quantum of frequency 0.293ν, travelling in the opposite direction. Although two quanta cannot coalesce, yet a collision of three quanta can give rise to two quanta with new frequencies and still satisfy (1), (2) and (3).

52. Quantum resonance and chemical reaction rate. R. M. LANGER, National Research Fellow, Bureau of Standards.—The theory of resonance in quantum mechanics leads to a suggestion as to the mechanism of chemical reaction which, applied to homogeneous unimolecular reactions, gives a simple, physically plausible picture. It is shown that only in the case of complex molecules is a unimolecular decomposition to be expected. The point is that if there is an equality of energy levels in several chemical bonds, resonance causes a circulation of energy among them and it is difficult to add energy to one above the resonance level without first "loading" the others. This can be done only through many collisions. Moreover, as soon as the several resonant bonds together have more than the dissociation energy for the weakest one, decomposition is possible without collision, but the mean time before decomposition will depend on the energy. The high temperature coefficient found experimentally fits in naturally, but the current motion of "activation," loses or rather entirely changes its significance. Those cases where this theory shows unimolecular reaction can occur turn out to be just the cases where the difficulty of maintaining the "rate of activation" disappears. The variation of specific reaction rate with pressure and the change of temperature coefficient for different members of a series (e.g. dimethyl and diethyl ether) can be interpreted.

53. The hydrogen molecular ion as a wave-mechanical perturbation of the helium ion. P. M. MORSE AND E. C. G. STUECKELBERG, Princeton University.—Unsöld, Heitler and London and others have studied the electronic levels in a diatomic molecule by considering the perturbations caused by the approach of two separated atoms. In the following calculation the molecular electronic levels are obtained by determining the perturbation caused by splitting the nucleus of a simple atom. In particular, the hydrogen molecular ion has been obtained from the helium ion and the electronic energy as a function of the nuclear separation gives a curve which checks with that calculated rigorously for the ground state by Burrau within the limits of validity of the method. The curves for the excited states, which Burrau could not obtain by his method, show clearly the "promotion of the electron" as predicted by Hund and Mullikan. That is, the state $n=2$, $l=1$, $m=0$ for the "united atom," goes to the state $n=1$, $l=0$, $m=0$ for the separate atoms. This method is also used in the study of the neutral hydrogen molecule.

54. A problem of Brownian motion. G. E. UHLENBECK AND S. GOUDSMIT, University of Michigan.—Gerlach investigated the rotation Brownian motion of a small mirror suspended on a fine wire (Naturwiss. 15, 15 (1927)). It follows from the theorem of equipartition that the average square deviation of the mirror will depend on the temperature alone of the

surrounding gas. Gerlach verified this for a large range of pressures (1 to 10^{-6} atm.). The analogy which we found that existed between this problem and the well-known treatment of the shot effect by Schottky, enabled us to give a more detailed theory of this phenomenon. If the displacement, registered during a time, long compared with the characteristic period of the mirror, is developed into a Fourier series, we found the square amplitude of each Fourier component to be a function of the pressure and molecular weight of the surrounding gas as well as of its temperature. The sum of those squares, however, is a function of the temperature alone. This explains why the curves registered by Gerlach at different pressures, though all giving the same mean square deviation, are quite different in appearance.

55. Reflection of soft x-rays. Jos. E. Henderson, Yale University, and Elizabeth R. Laird, Mount Holyoke College.—The reflecting power of glass for soft x-rays at glancing angles up to 20° has been studied. General radiations from a nickel target excited by the stopping of electrons, whose velocity ranged from 100 to 4000 volts, was used. Total reflection, sharply defined, such as exists in the hard x-ray region is found not to exist in this region. The curves for all voltages exhibit a continuous decrease in reflecting power with increasing glancing angle as was reported earlier (Proc. Nat. Acad. Sci., Oct., 1928). The unexpected crossing of the curves described there has been investigated with greater precision and the effect definitely found to exist. The lower voltage radiation is less reflected at small angles (under about 4°) than the higher voltage radiation. At larger angles the lower voltage radiation is more reflected than the higher voltage radiation. A theory is proposed explaining the continuous decrease in reflecting power with increasing glancing angle and the crossing of the curves.

56. Dispersion of soft x-rays in glass and platinum. Elmer Dershem, University of Chicago.—The refractive indices of a sample of glass, density 2.50 gm/cc, composition unknown but evidently containing Al_2O_3, were determined by the total reflection method for wave-lengths from 4.2 to 9.15A. Plotting $1-\mu=\delta$ against λ reveals lowered values of δ at the K absorption limits of silicon and aluminum. The maximum critical glancing angle observed was 1°20′ at 9.15A. The corresponding value of δ being 2.7×10^{-4}. These measures were observed to be affected by surface conditions. Preliminary measurements in the M region of platinum previously reported, (Phys. Rev. **31**, 305 (1928)), have been repeated in more detail and the resulting dispersion curve shows three marked minima in values of δ, one at a wave-length corresponding to a mean of the wave-lengths of the M_I and M_{II} limits, another at the M_{III} limit and the third at a mean of the M_{IV} and M_V limits. The region of anomalous dispersion extends over a considerable frequency range on either side of an absorption limit. Hence the minima due to limits having small frequency separations are not easily resolved. The major part of this work was done at the University of California.

57. The crystal structure of tri-calcium aluminate. Wheeler P. Davey and F. A. Steele, Pennsylvania State College.—Tri-calcium aluminate has cubic symmetry. The density and the diffraction pattern of the powder show that the unit of structure contains $9CaO.3Al_2O_3$. The theory of space groups permits about 1500 cubic structures containing 9A, 6B, and 18C. The packing radii of the ions involved make all but 40 of these structures impossible unless we grant a linear compression of at least 10 percent beyond what is found in other compounds. Of these 40, 37 show calculated values of intensities widely different from those found by experiment. The remaining three structures are very similar to each other. The best fit gave Ca at 8*c* and 1*a*, Al at 3*a* and 3*b*, and O at 6*d* and 12*f* (Wyckoff nomenclature). None of the three structures show any evidence of units of CaO, AlO_3, or Al_2O_3. The oxygen ions are symmetrically shared by both Ca and Al. It is proposed to call this type of compound "mixed ionic." The side of the unit cube is 7.624A.

58. Satellites of certain x-ray lines. F. K. Richtmyer, Cornell University.—It has been long known that accompanying many x-ray lines, usually on their short wave-length side, are found fainter lines which do not fit into the usual x-ray energy level diagrams and which, until we have an acceptable theory of their origin may be called "satellites." Because of their probable bearing upon the problem of the origin of spectra, it is desirable to secure, if possible,

more precise data as to wave-length, excitation potentials and relative intensities of these satellites. Such a study has been initiated and the present paper is a preliminary report concerning the wave-lengths of certain of these lines. Measurements of the satellites of $L\alpha_1$, $L\beta_1$, $L\beta_2$ and $L\gamma_1$ for the elements Rb(37) to Sn(50) have been made from plates taken by the author and R. D. Richtmyer in Professor Siegbahn's Laboratory. $L\alpha_1$ has five satellites (possibly seven): $L\beta_1$ has three; $L\beta_2$ has three (possibly five); and $L\gamma_1$ has two. The results confirm the empirical law, previously proposed by the author for the satellites of $K\alpha$ (Phil. Mag. **6**, 64 (1928)), that the square root of the frequency difference between a satellite and its parent line is a linear function of atomic number. (The author acknowledges assistance from the Heckscher Research Council of Cornell University.)

59. Fine structure of scattered x-rays. DANA MITCHELL AND BERGEN DAVIS, Columbia University.—Examination of Mo$K\alpha$ rays scattered from aluminum at approximately 90° has been made by the method used with graphite and reported at the last April meeting of this society (Phys. Rev. **31**, 1119; **32**, 331 (1928)). Four lines attributable to Mo$K\alpha$ have been found in the following positions: Mo$K\alpha_1$ unmodified, Mo$K\alpha_2$ unmodified, one between Mo$K\alpha_1$ and Mo$K\alpha_2$ and one on the long wave-length side of Mo$K\alpha_2$. These two shifted lines correspond to about 2.3 and 5.6 X.U. from Mo$K\alpha_1$. If the loss of energy of these scattered Mo quanta is correctly described by $Ve = h\nu - h\nu'$ the energy levels of aluminum can be determined from the convenient form $\Delta\lambda = \lambda^2/(\lambda_s - \lambda)$ where $\Delta\lambda$ is the wave-length shift. These give two of the absorption limits of aluminum as 57 ± 6 and 136 ± 6 equivalent volts. At the date of writing the aluminum K shift is 69 X.U. Preliminary data using Be gives an anti Stokes L and Stokes K.

60. Gamma and cosmic rays. J. A. GRAY AND A. J. O'LEARY, Queen's University.—Experiments with gamma-rays have led to the following conclusions: (1) Accurate values of the variation of intensity of cosmic rays with height are not obtained by assuming that they travel in straight lines without scattering and have an absorption coefficient independent of depth. This method of calculation leads to too high a value for the intensity near the surface of the atmosphere. (2) Wave-lengths, obtained by assuming that Dirac's formula connecting scattering coefficients with frequency is correct, are too long. (3) The soft or local rays observed in cosmic-ray experiments are not produced by the hard rays. There is some evidence that part of the hard radiation is of terrestrial origin also. It is difficult to make the correction due to the local rays in balloon and other experiments. The use of the results of such experiments without this correction leads to too high a value for the total intensity of cosmic rays.

61. The significance of measurements of ionization in closed vessels in relation to cosmic radiation. W. F. G. SWANN, Bartol Research Foundation of The Franklin Institute.—A cosmic ray of absorption coefficient 0.1 per meter of water could produce, by the complete utilization of its energy, about 5.5×10^6 ions. If we assume that, on the average, the rays produce 1.4 ions per cc per second at sea level only one cosmic ray could be absorbed in 4000 seconds in a vessel of 1 liter capacity. Most of the ionization which this ray is capable of initiating through its secondary radiation is of course produced outside of the actual air in the vessel, and the ionization produced in the vessel comes mainly from secondary radiation initiated by the absorption of primary rays in the vessel wall. The development of these considerations leads to the following conclusions in relation to variation of residual ionization with pressure. If N is the ionization which would be produced at standard pressure in the volume of the vessel by the cosmic radiation but with the walls absent, the increase per atmosphere in the neighborhood of one atmosphere is equal to the ionization at one atmosphere, and is greater than N while the increase per atmosphere at sufficiently high pressures attains a constant value which is equal to the ionization produced in the volume of the vessel at the higher pressure by the cosmic rays and their secondary radiations absorbed in that volume alone at one atmosphere.

62. The "anomalous dispersion" of electron waves by nickel. C. J. DAVISSON AND L. H. GERMER, Bell Telephone Laboratories, Inc.— Our experiments on the reflection of electrons (Proc. Nat. Acad. **14**, 619 (1928)) indicate strongly that electron waves are refracted on passing into a metal. The dispersion curve for nickel which we constructed from the data of these

experiments shows elaborate and surprising features. In particular, near $\lambda = 1.3$A this dispersion curve has a discontinuity suggestive of optical anomalous dispersions. Further evidence of this phenomenon has been found in a re-examination of the data of our earlier experiments on diffraction beams of the Laue type (Phys. Rev. **30**, 705 (1927)). Only one of these beams occurs near the anomalous region about 1.3A. This beam is first detected at $\lambda = 1.37$A; it increases in intensity to $\lambda = 1.33$A; then becomes very weak through the anomalous region; and finally grows rapidly stronger again, reaching its maximum intensity at $\lambda = 1.19$A. With further decrease in wave-length this beam steadily decreases in intensity in the manner characteristic of other beams of the Laue type, finally vanishing at $\lambda = 1.07$A. The condition for an intensity maximum is that λ/μ have the value $(2d \cos\theta)/n$. It looks as if, with μ changing rapidly with λ, there are two values of λ (1.19A and 1.33A) for which this relation is satisfied, and the beam really occurs twice.

63. The reflection of hydrogen atoms from crystals. THOMAS H. JOHNSON, The Bartol Research Foundation of the Franklin Institute.—The experiments published under this same title in the Journal of the Franklin Institute, Sept. 1928, have been continued with the following new results. Quantitative measurements of the intensities of the specularly reflected hydrogen atom beams from a cleaved surface of a hot crystal of rock-salt have been made with the results given in the table.

Angle from grazing	5°	10°	15°	30°	45°	60°
Intensity of reflected beam: intensity of incident beam	.01	.0097	.0096	.0087	.0041	.0021

Although no specular reflection was found from KCl under the conditions of the earlier work, such beams have now been found and they vary in intensity with the angle about as the beams reflected from rock salt but they are at least ten times weaker than the latter. To test the possibility that the probability of specular reflection depends critically upon the velocity of the atom, the specularly reflected beam at 20° from grazing from one rock-salt crystal was again reflected at the same angle from a second crystal. Since no specular beam appeared from the second crystal during an exposure of more than ten times that required to obtain an observable record from the first crystal it is concluded that the velocity selection in the specular beam cannot be very pronounced.

64. Angular scattering of electrons in gases. GAYLORD P. HARNWELL, Princeton University.—A slightly modified form of the apparatus described in an earlier paper (Proc. Nat. Acad. **14**, 564 (1928)) has been used to repeat and extend the results reported there. The negative results that had been obtained for the scattering of fast electrons through large angles have been confirmed. Evidence of the scattering of electrons, whose energies are in the region from 50 to 150 volts, through small angles has been obtained. It has been found that the angular region, through which electrons that have lost no energy are scattered, is very limited. In very few cases does this region extend more than ten degrees on either side of the original beam. As the energy of the primary electrons increases this region tends to become still narrower. The evidence also indicates that for electrons with an energy of 100 volts very few of those which have suffered an inelastic impact remain in the original beam. However, they are only deflected through angles of a few degrees. As the energy of the primary beam increases these electrons also tend to be deflected through smaller angles.

65. The Compton effect produced by standing electromagnetic waves according to wave mechanics. MILDRED ALLEN, Bartol Research Foundation.—If x-rays, in the sense of classical electromagnetic theory, pass out from a point and are reflected by two crystals so as to form two oppositely directed beams of electromagnetic waves, the net result will be a system of stationary electromagnetic waves. The results to be predicted by the wave mechanics for the Compton effect in this case are not immediately obvious, particularly in view of the absence of a resultant electromagnetic momentum for the standing waves. On submitting the matter to calculation, it turns out that, to a first approximation, the solutions for the vector and scalar potentials resulting from the $\psi\bar{\psi}$ distribution divide themselves into two parts, corresponding to the two

oppositely directed electromagnetic waves; and it results from this that where the interpretation of the wave mechanics solution is made in terms of probabilities of Compton transitions, the result is the same as though each of the oppositely directed waves acted independently of the other. The paper concludes by sketching the relation between the general theory of the Compton effect and Schroedinger's original theory made in terms of the reflection of the electromagnetic waves, according to the Bragg law, from gratings generated by the $\psi\bar{\psi}$ distributions.

66. Lattice energetics of thermal vibrations in solids. R. H. CANFIELD, Naval Research Laboratory.—Assuming that the energy of a space-lattice may be expressed, as by Mie, Grüneisen and others, in terms of the "average distance" of an atom from its neighbors, a formula is derived for the upper limit of amplitude of thermal vibration, and hence for the width between branches of the energy curve at room temperature. This largest amplitude, ρ equals $C_v K/9\alpha\bar{r}^2$, where C_v equals specific heat per atom, k is compressibility, α is the coefficient of linear expansion, and $\bar{r}$ is the cube root of the volume per atom. If the slope of the energy curve where it intersects the room temperature axis is much larger at the intersection where $r<\bar{r}$ than it is where $r>\bar{r}$, then ρ as given above may be taken as the true half-width of the energy curve. It is shown that the calculated half-widths of the curves for fourteen cubic metals account for their falling into body- or face-centered lattices; that the calculated frequencies agree with the demands of the quantum theory of specific heats; and that a possible rule for the melting point may be that it occurs when the accoustic wave-lengths become as small as twice the distance between atoms.

67. The temperature coefficients of resistance of low melting point metals in the solid and liquid states. W. B. PIETENPOL AND H. A. MILEY, University of Colorado.—The authors have given a preliminary description (Phys. Rev., **30**, 697 (1927)) of a unique method of measuring the resistance-temperature coefficients of low melting point metals through the solid and liquid states. The difficulties in the way of making such measurements have been largely eliminated by employing oxide films as containers for the molten metals. In the present article the resistivity-temperature curves are shown for the metals (Pb, Sn, Zn, Bi), and the temperature coefficients of resistance are given for 10° intervals throughout the range 20°C to above 550°C. The resistance-temperature coefficients of zinc above the melting point are found to be positive instead of negative as reported by E. F. Northrup and V. A. Suydam (Jour. Frank. Inst., **175**, 153 (1913)). The coefficients of these metals are all positive except those for bismuth in the regions 160°–180°C and 225°–275°C. The negative coefficients may be explained in the first case as due to a transformation in the crystalline metal, and in the second case they are due to the decrease in the resistivity of the bismuth as it approaches the melting point and passes from the solid to the liquid state.

68. Improved methods of exciting Raman spectra of scattered radiation. R. W. WOOD, Johns Hopkins University.—The mercury arc suffers from the disadvantage that no single line can be used for excitation even by the use of filters (4358 is triple, and 4046 cannot be separated from 4077). On this account the spectrum lines cannot be identified, until all λ's are measured and the frequency differences calculated. The author has employed a spiral helium tube surrounding a tube of black glass (colored by nickel oxide) which is very transparent to the strong helium line 3888. Within this tube is the tube containing the liquid, or the tube of black glass may have a window of clear glass fused to its end, and be employed for holding the liquid. In this way one obtains a Raman spectrum by strictly monochromatic excitation. A wave-length scale graduated for infra-red frequencies (i.e. in μ's) can be prepared and placed in coincidence with an enlargement of the spectrum. In this way the infra-red absorption bands can be determined without any wave-length measurement or calculations.

69. A rational proposal for the control of a hurricane. WM. S. FRANKLIN, Mass. Inst. of Technology.—The great Florida-Porto-Rico hurricane of mid-September was preceded by a widely extended state of instability of the atmosphere with warm moist air near the ground and colder air above, and if this state of instability could have been "touched off" at several places in the neighborhood of the Florida coast the local energy of this unstable state might have been

frittered away in several mild storms so that there would have been no energy left to feed the great storm when it reached the Florida region. It is thus conceivably possible to control a hurricane. The question is however; is it humanly feasible to "touch off" an unstable atmospheric state and start a storm? No one knows the answer to this question, and although I am inclined to think it is not feasible, I believe that a corps of observers should be assigned to the Porto Rico and Florida region to make continuous studies of the vertical distribution of temperature, humidity, and wind velocity in the atmosphere so as to capture data for a pre-hurricane state. Then from these data one could calculate, by the method of L. F. Richardson, how much of an upward impulse would need to be given to a specified volume of air in order to "touch off" a storm. If this needed amount of impulse should be only moderately large it might then be worth while to build an air-impulse gun to try the "touching off" of a storm, and then make an attempt to fritter away the energy of any atmospheric state that might arise and threaten to form a severe hurricane.

70. Heat transmission of air space by hot plate method. L. F. MILLER, University of Minnesota.—The hot and cold plate apparatus, with guard ring, taking foot square layers of insulating material, was used. The double layers each side of the hot plate, consist of two sheets each 6.55 mm thick, of a firm rag felt insulation between which uniform layers of air space of increasing thickness may be introduced by stacking small pieces of cork at eight or ten different points. Designating the heat transmission as, h_s for the two felt sheets in immediate contact with no air space, h_a for the various thicknesses of air layer, and H for the felt sheets and air layer combined, then from the relation $1/H=1/h_s+1/h_a$, the value for the different air layers h_a can be calculated, since H and h_s are measured in the apparatus. As the thickness of air space increases (convection presumably building up) h_a decreases along a curve which flattens out and has a minimum for an air layer about 20 mm thick. If we calculate a coefficient of thermal conductivity for each of these air layers and plot these values, the curve runs into a value of 5.68×10^{-5} calories per sec per cm³ per deg C, as thickness of air layer approaches zero where convection vanishes. This checks with the accepted value of the coefficient of thermal conductivity of air.

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